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Division of Chemical Science

(IZVESTIYA AKADEMY NAUK SSSR)

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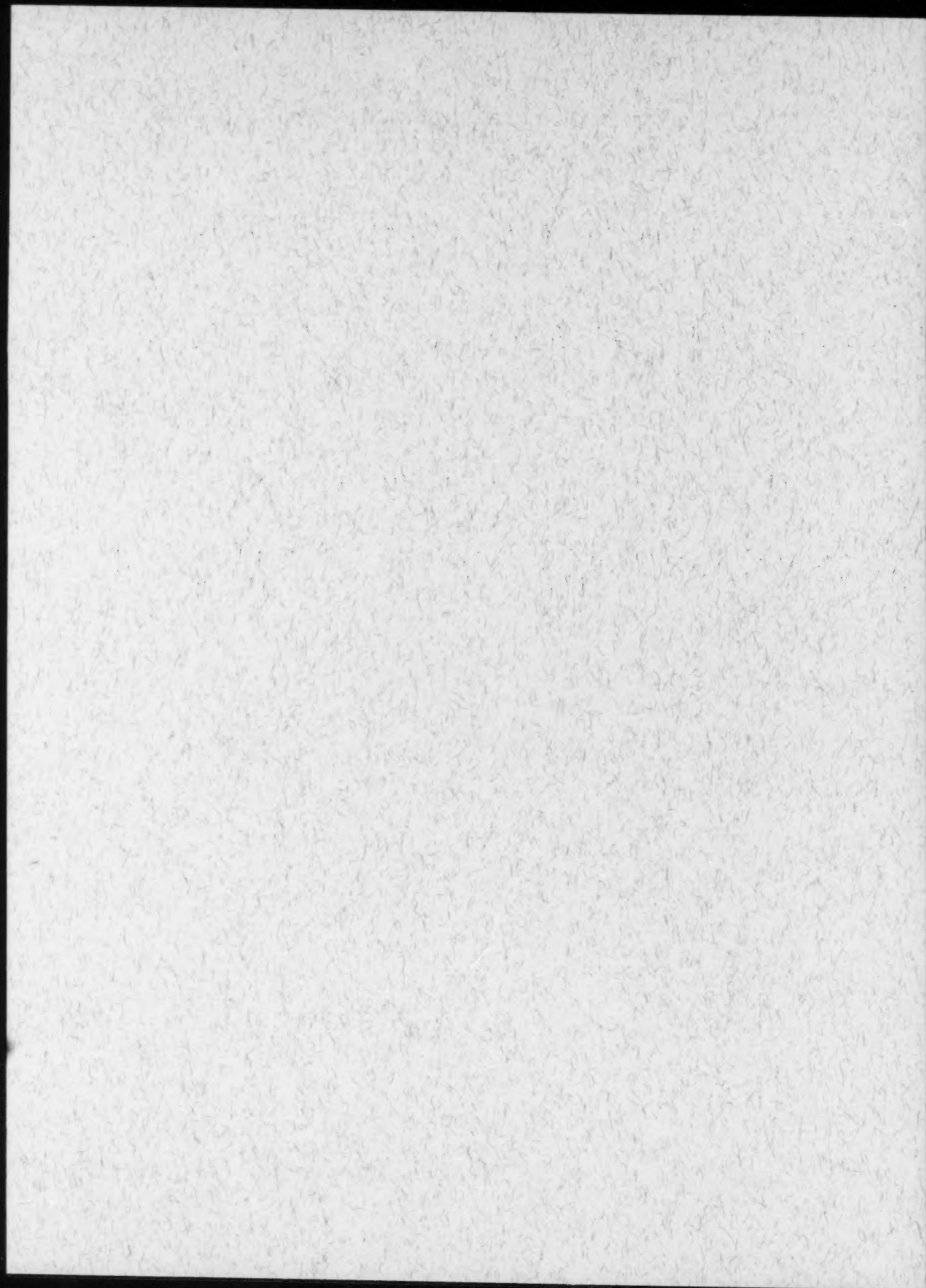
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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LEIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.



Salutation to Academician Aleksandr Vasilyevich Topchiev

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences, cordially greet you on the occasion of your fiftieth birthday.

Your extensive and profound investigations on the nitration of hydrocarbons, reactions of alkylation and polymerization with the participation of catalysts based on boron trifluoride, and synthetic processes of great prospective significance based on petroleum are widely known. You are able to combine successfully this work on major problems of organic chemistry with extensive work on the organization of science.

We wish, dear Aleksandr Vasilyevich, that you may enjoy good health and make continuing progress in your creative work.

Division of Chemical Sciences of the Academy of
Sciences of the USSR

and

Editorial Board of the Bulletin of the Academy of
Sciences of the USSR, Division of Chemical Sciences

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GENERAL AND INORGANIC CHEMISTRY

EXPLORATORY INVESTIGATIONS ON THE CHEMISTRY

AND TECHNOLOGY OF FERTILIZERS AND SALTS

COMMUNICATION 2

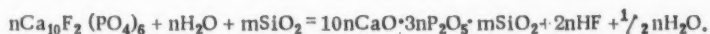
S. I. Volfkovich

(Paper read at a Joint Session of the Division of Chemical Sciences of the Academy of Sciences of the USSR, Moscow University Chemistry Department, and the Institute of Fertilizers and Insectofungicides, November 2, 1956)

New Manufacturing Methods

Apart from the manufacturing methods mentioned in the first communication, we have recently carried out exploratory work to determine the possibility of carrying out the following technological processes: hydrothermal treatment of phosphates in a "fluid bed" and in the melt with natural gas; fusion of phosphorites containing an appreciable amount of magnesium and silica (e.g., kara-Tau phosphorites) to give phosphate-magnesia fertilizer; thermal dissociation of defluorinated phosphate to give phosphoric oxide; chlorination of phosphorites to give H_3PO_4 and HCl ; treatment of ferrophosphorus with chlorine; preparation of zinc phosphide by reduction of zinc phosphate with carbon; absorption of gases containing fluorine compounds with solid calcium and sodium carbonates, nepheline, etc.; and enrichment of Kara-Tau phosphorites by means of sulfur dioxide.

The new technological process of hydrothermal treatment of natural phosphates with the object of freeing them from fluorine and converting the phosphate into the citrate-soluble form is, in the scheme that we have studied, carried out in a tube furnace at 1400–1500° in presence of steam and added silica in accordance with the overall equation:



The investigation of this process has been partially described in a paper by the author, V. Illarionov, and D. Reimen in the journal *Chemical Industry*, 1954, No. 4.

As the hydrothermal treatment of phosphate is a heterogeneous process, the rate of which is determined by the rate of diffusion of gas to the surface of the solid phase through a laminal layer of gaseous products, in 1950–1951, working at Moscow State University, the author, A. M. Malets, and I. M. Meskin carried out experiments on the defluorination of an apatite concentrate in a suspended semisuspended condition. These experiments showed that, at 1450° with a steam concentration of 10%, the apatite concentrate was defluorinated to the extent of 95% in 12–20 seconds, i.e., many times faster than in a rotary furnace with internal heating.

With the fusion of the apatite concentrate, heated to 1540°, the rate of the process was considerably increased; the difficulties associated with the sintering of phosphate particles at high temperature were then removed. As a result of these experiments it was proposed to a shaft furnace with atomization of the phosphate so that it would interact vigorously with the combustion products of liquid or gaseous fuel. Owing to fineness of dispersion and renewal of the phosphate surface, or to the use of a higher temperature with consequent fusing of the charge, a furnace of much smaller dimensions than a rotary cement furnace would cope adequately with the process. These experiments indicated that very promising results were to be expected

from the use of furnaces of the cyclone type designed by Prof. Knorre or of furnaces with a suspended or semi-suspended layer of reactants for the hydrothermal treatment of phosphates. It is planned to carry out appropriate experiments on these lines in the Furnace Technology Laboratory of the Moscow Energy Institute under the direction of Prof. N. A. Semenenko working jointly with NIUIF (Research Institute of Fertilizers and Insectifungicides) and Giprokhim (State Institute for the Planning of Projects in the Heavy Chemical Industry).

Tentative thermodynamic calculations of I. M. Meskin showed that the high temperature necessary for the defluorination of apatite is associated with the high activation energy for this reaction. Maximum defluorination is favored by reduction in the concentration of hydrogen fluoride, i.e., by constant removal of gaseous reaction products, and, to a less extent, by increase in the concentration of steam (10–14%). Steam must be fed at the rate at which it interacts with apatite in order to ensure as complete removal of HF as possible and therefore to maintain the system as far as possible from the equilibrium state. Experiments of I. M. Meskin and A. Yu. Kizas (NIUIF) showed that it is possible to carry out the defluorination of apatite with the combustion products of methane. These experiments point to the desirability of using natural gas as a source of heat and steam.

In a study in 1954–1955 of the part played by magnesium in hydrothermal treatments of natural phosphates, we found that in presence of increased amounts of magnesia and silica such phosphates pass into the citrate-soluble state when fused in absence of steam. Laboratory experiments carried out in NIUIF by R. E. Remen, V. V. Illarionov, and E. I. Petrova showed that an assimilable phosphate fertilizer with a degree of phosphate decomposition of 90–95% can be obtained in a thin layer of fused Kara-Tau phosphorite containing considerable amounts of SiO_2 and MgO , even without special additives and defluorination. These extremely interesting results must be verified in a cyclone-stoking furnace heated by coal dust and in a shaft furnace working with solid fuel. These experiments again confirm that complete removal of fluorine is not essential in the manufacture of fused magnesian phosphates.

Our attention has long been attracted by the reaction of thermal dissociation of calcium phosphates with direct formation of phosphoric oxide. The existing method of obtaining phosphoric oxide, phosphoric acid, and phosphate fertilizers by the electrothermal sublimation of phosphorus demands not only heating of the charge (phosphate, quartz, lime, etc.) to about 1500° by means of electric energy, but also a large amount of valuable carbonaceous reductant (coke or anthracite), after which the resulting phosphorus is burnt with the evolution of much heat. In experiments carried out at our initiative by Yu. M. Rabinovich in 1936 in NIUIF on the thermal dissociation at 1500° in a vacuum of tricalcium phosphate in admixture with silica, it was shown that 95–96% of the phosphorus could be isolated in the form of phosphoric oxide without use of a reducing agent. In a stream of air the reaction proceeded at $1600\text{--}1700^\circ$. At high temperature silica behaves as a strong acid and vigorously displaces phosphoric oxide. We are now returning to a study of this problem, our task being to make a more detailed investigation of the part played by the vacuum and the introduction of silica and other additives.

In chemical technology, various processes of thermal dissociation of natural raw materials are used in order to obtain the corresponding acid anhydrides and metal oxides. The thermal dissociation of limestone into carbon dioxide and lime finds extensive industrial application. Industrial experience has shown the feasibility of the thermal dissociation of gypsum or anhydrite into sulfur dioxide and lime. In the roasting of arsenic-containing ores of nonferrous metals, arsenious oxide is obtained in the gas phase. When we consider the rapid progress of technology, as a result of which oxygen is being widely used in manufacture, great progress is being made in "fluid-bed" methods, and vacuum-furnace and other advanced techniques are being used, there remains no grounds for doubt in the practical pertinence of the problem of the thermal dissociation of phosphates or the displacement of phosphoric oxide from them.

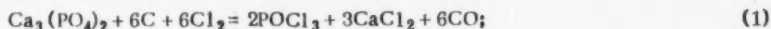
If this problem can be solved in an economically favorable manner, then there will be no serious difficulties in the binding of the resulting phosphoric oxide with ammonia and potassium, calcium, and magnesium compounds to give high-concentration metaphosphate and pyrophosphate fertilizers. Methods for these syntheses were proposed years ago by E. V. Britske and coworkers. It is very probable that it will be found expedient in the future to utilize atomic energy and other sources of energy for such power-consuming, high-temperature processes.

In considering thermal methods of treating phosphates, we cannot exclude the possibility of further considerable improvement and cheapening of the electrothermal method of sublimation of phosphorus, both by

reduction in the consumption of electrical energy and by the combination of this process with other manufacturing processes with rational utilization of the composition and thermal energy of the waste gases (carbon monoxide). It is of interest to note the idea of a combined electric and flame furnace (in accordance with the project of E. V. Britske, M. N. Bolotin, and the German scientist Mener) and other variants.

Some physicochemical and technological investigations (calculations and experiments) have been devoted to the chlorination of natural phosphates. Unlike some previous investigations by other authors, in which chlorine was used to remove iron and aluminum impurities, for the preparation of phosphoryl chloride, and also for the solubilization of the phosphate, our work has had the object of preparing phosphoric and hydrochloric acids from apatite in two main manufacturing stages:

a) treatment of phosphate with chlorine in presence of carbon:



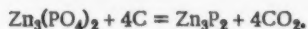
b) hydrolysis of phosphoryl chloride:



Owing to the exothermicity of reaction (2), gaseous hydrogen chloride is driven completely from the phosphoric acid, which can be obtained in high concentration (up to 90–94% H_3PO_4) and comparatively pure. At 720–750° the yield of phosphoryl chloride obtained from an apatite concentrate in accordance with Equation (1) attained 90%, and the extent of hydrolysis in accordance with Equation (2) was 100%. The results of this work enable us to pass to the detailed development of the technological scheme of the process. Laboratory and calculation work has been carried out in NIUIF by V. V. Illarionov, R. E. Remen, T. I. Sokolova, T. A. Banshchikova, A. S. Lachkova, and myself.

Experiments on the chlorination of ferrophosphorus showed that it is possible to convert it almost completely into phosphorus trichloride and ferric chloride at 400–450°. Addition of common salt to the reaction products permits phosphorus trichloride to be driven off almost completely (experiments by V. A. Skvortsov). By reaction of ferrophosphorus with sulfur or iron sulfide at 700–1100° it is possible to obtain phosphorus sulfides in about 95% yield. Information on the reactions occurring has been obtained by experiments and thermodynamic calculations carried out by V. V. Illarionov and T. I. Sokolova.

We have already mentioned our experiments on the preparation of zinc phosphide. In view of the clumsiness, high power consumption, and expense of the process now used (fusion of red phosphorus with zinc in a heated rotating reactor), R. E. Remen and coworkers carried out a series of experiments on the preparation of zinc phosphide by the reduction of zinc phosphate with carbon in accordance with the equation:



This process avoids the use of expensive elementary phosphorus. The experiments showed that the method was promising and required only the presence of phosphoric acid and zinc or zinc oxide. Another method that we have studied for the preparation of zinc phosphide consists in the interaction of gases coming from the electric furnace in the sublimation of phosphorus and containing concentrated carbon dioxide with zinc oxide. The study of various methods for the preparation of zinc phosphide is to be explained by the necessity of greatly expanding production of this effective means of combating rodents, which cause a great deal of harm in agriculture.

The fluorides and fluosilicates used for the impregnation of wood as insecticides and antiseptics are now prepared by the absorption of gaseous HF and SiF_4 in water or alkaline-salt solutions, followed by the operations required to convert the solutions into solid products. In conjunction with M. G. Gabrielova, I have tried out analogous "dry" processes for the preparation of sodium and potassium fluosilicates: absorption of gaseous silicon tetrafluoride by solid sodium and potassium carbonates; and for the preparation of calcium fluoride, reaction of HF and SiF_4 with CaCO_3 . As experiments with chalk showed, reaction between HF and CaCO_3 proceeds fairly satisfactorily, but reaction between SiF_4 and CaCO_3 goes much less satisfactorily. As would be expected, the course of these reactions between a gas and a solid is greatly affected by the dispersity, microporosity, and extent of surface renewal of the calcium carbonate, and also by the composition and structure of the latter. We are at present making a detailed investigation of this process with calcium carbonate in the suspended state.

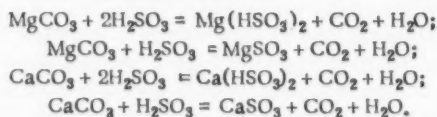
Foreign work in this direction has provided information on the conditions for the interaction of HF with comparatively coarse limestone particles. If work on the design and operation of a continuous reactor confirms its technical and economic efficiency, then it will be desirable to try out analogous processes for the absorption of other gases, such as sulfur dioxide and trioxide and oxides of nitrogen.

In our study of the interaction of gaseous fluorine-containing compounds with alkaline compounds we examined the possibility of using nepheline for this purpose. Nepheline is a complex sodium potassium aluminosilicate found in large amounts in association with Khibin apatite and as deposits in various other districts. Nepheline is readily decomposed, even in weak acids, and it was therefore of interest to determine the possibility of using it for the neutralization of the weak solutions of hydrofluosilicic and hydrochloric acids obtained in the treatment of phosphates in the preparation of superphosphate and other phosphate fertilizers. Experiments of R. E. Remen and E. I. Petrova confirmed the possibility of using nepheline for this purpose with subsequent utilization of the product in the cement, glass, and other industries and for the preparation of sodium and potassium fluosilicates and fluorides, etc. Nepheline was found to be suitable for the treatment of acid effluents and for the neutralization of the free acidity of ordinary and double superphosphates. Work carried out at our suggestion by the staff of NIUIF has confirmed the possibility of using nepheline for the neutralization of the free acidity of superphosphate. However, as the total P_2O_5 content of the superphosphate is somewhat reduced by this treatment, nepheline has not found application for this purpose. It must be taken into account, however, that the aluminous and siliceous gels formed in the decomposition of nepheline aid in the granulation of the superphosphate and improve its physical properties, and there are various cases, therefore, in which the use of nepheline may be found advantageous.

In view of the fact that Kara-Tau phosphorites contain considerable amounts of magnesium, in 1948 we proposed their chemical enrichment with the aid of sulfur dioxide or sulfurous acid, which was subjected to preliminary trials by R. E. Remen and was later investigated at the Moscow State University by E. V. Povarkov. Processes for the chemical enrichment of Kara-Tau phosphorites and of apatite ores were studied still earlier in NIUIF, for hydrochloric, nitric, and sulfuric acid treatments by A. A. Sokolovsky, A. I. Shereshevsky, A. I. Loginova, and others, and later for treatments with sulfurous and sulfuric acids by M. L. Chepelevetsky, E. B. Brutskus, and others. The specific feature of this problem consisted in the necessity of removal of considerable amounts of magnesium and, to a certain extent, calcium carbonates, associated in the form of dolomite, from the Kara-Tau phosphorite. These impurities make the treatment of phosphorites for the production of superphosphate and concentrated phosphate fertilizers much more difficult and expensive, because they make increased consumption of acid necessary. The presence of soluble magnesium salt in the superphosphate increases hygroscopicity and caking, and its presence in extraction phosphoric acid makes the further conversion into double superphosphate difficult.

The application of sulfur dioxide or sulfurous acid was attractive to us not only because this acid is less active than most of the other common mineral acids and so is able to act on carbonates without touching phosphates, but also because it is cheaper than the other acids, being obtained as a by-product, and sometimes as a waste product, in nonferrous metallurgical works (copper and metalloids). Much of the sulfur dioxide bound in the process of dissolution of dolomite can be brought back into the process by heating the solution obtained or by displacement with another acid. Still earlier, R. E. Remen carried out some preliminary experiments on the enrichment of Kara-Tau phosphorites with carbonic acid, but they did not give satisfactory results because carbonic acid is very much less active than sulfurous acid. As is well known, in this respect H_2SO_3 stands between HCl , HNO_3 , H_2SO_4 , H_3PO_4 , on the one hand, and H_2CO_3 , on the other. The degrees of dissociation of the acids in 0.1 N solutions at 18° are: HCl - 92%, HNO_3 - 92%, H_2SO_4 - 58%, H_3PO_4 - 27%, H_2SO_3 - 34%, H_2CO_3 - 0.17%.

Reaction of sulfurous acid with magnesium and calcium carbonates results in the formation of magnesium and calcium sulfites and bisulfites, which pass into solution:

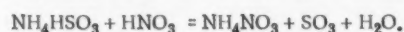
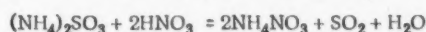
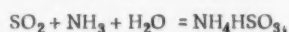
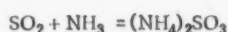


By adjustment of the amount and concentration of the sulfurous acid and the duration of interaction with the ore, conditions can be obtained which ensure that the phosphate minerals do not pass into solution, or

dissolve only very slightly. Experiments by E. V. Povarkov established the possibility of enriching Kara-Tau phosphorite from 27% to 30--31% P_2O_5 with reduction in CO_2 content from 7% to 0.7%; decomposition of dolomite exceeded 90%, but practically no decomposition of the phosphate occurred. The experiments established provisional standards of procedure, acid concentration, and duration of treatment. Independent of this work of M. L. Chepelevetsky and E. B. Britskus, thorough investigations on the decomposition of Kara-Tau phosphorites with sulfurous and sulfuric acids were carried out in NIUIF.

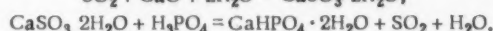
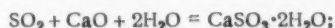
Apart from the use of sulfur dioxide for the enrichment of phosphorites, we tried methods of concentrating sulfurous gases with simultaneous formation of phosphorus and nitrogen fertilizers in a single complex process. The main object of these investigations was the utilization of weak sulfurous gases in the wastes from metallurgical furnaces and thermally operated electric power stations working with low-quality coals containing much sulfur. We based our process on the possibility of absorbing weak sulfurous gases with ammonia or lime with subsequent displacement of sulfur dioxide from the resulting salts by means of nitric or phosphoric acid. Such processes have been studied before, but they were not applied in practice.

One process is based on the reactions:



These equations show that the final products should be ammonium nitrate and concentrated sulfur dioxide. This method was proposed by Z. P. Rozenknop, A. M. Dubovitsky, and myself and has been described in some short notes*.

Another process is based on the overall reactions:



Here, the final products are dicalcium phosphate ("precipitate") and concentrated sulfur dioxide. Preliminary tests on this method were made in NIUIF on the initiative of A. G. Pavlovich and M. M. Kobrin as long ago as 1939.

The ammonia method was tried out by N. Yu Lyuboshits, graduate student of the Moscow State University, who showed that in this process, together with the concentrated sulfurous gas, it is possible to obtain either ammonium nitrate (as a fertilizer) or ammonium sulfate-nitrate close in composition to fertilizers of the "lein" saltpeter type. A detailed laboratory and pilot-scale study of this process has been carried out in NIUIF under the supervision of Z. P. Rozenknop and N. A. Vasilenko.

The process of preparing "precipitate" and concentrated sulfur dioxide gas was tried out by V. A. Serebryakova, graduate student of the Moscow State University, who demonstrated the possibility of obtaining a high-strength phosphate fertilizer containing part of the P_2O_5 in a water-soluble and part in a citrate-soluble form. The treatment of calcium and magnesium sulfites with phosphoric acid was studied in detail in NIUIF by M. L. Chepelevetsky and E. B. Brutskus as a stage in the process of enriching Kara-Tau phosphorites with sulfurous gases.

Development of Theoretical Ideas

Most theoretical questions require profound calculations and experimental investigations for their solution. In this section, therefore, we shall consider only a small part of the exploratory investigations. We are concerned here with three lines of investigation:

- a) theoretical matter concerned with the manufacture and application of phosphate fertilizers;
- b) crystal chemistry of ammonium nitrates and other nitrogenous salts;
- c) methodological basis of pilot-scale experimental work.

* Communications to the Mendeleev All-Union Chemical Society, 1948, No. 2, and others.

In recent years there have been more and more investigations in chemical, physical, and biological fields with the object of determining the relationship between physiological activity, composition, and structure of chemical compounds. One such problem consists in the determination of the relationship between the effectiveness of the various forms of phosphates, their compositions, and their structures. Agrochemistry and plant physiology have accumulated extensive experimental material which, however, has been generalized and analyzed only to a very slight extent from the point of view indicated. Hence, in NIUIF work on this has been undertaken by a team of chemists, agrochemists, x-ray analysts, and other specialists; it is already in its third year.

Various chemically pure phosphates and silicophosphates synthesized by chemists and characterized by crystallographic, x-ray, and thermographic parameters are being investigated systematically by agrochemists by the vegetational method with application of radioactive isotopes.

This theoretical work has already given interesting results. Thus, the conditions have been determined for the retrogradation and assimilation of the P_2O_5 of various phosphates and silicophosphates during prolonged interaction with water. Phosphates that do not contain bound silica readily pass into a hydroxyapatite that is not readily assimilated by plants. In silicophosphates this change is greatly retarded. Samples corresponding in composition to basic slag and nagelschmitite preserve their structures unchanged in this treatment. The stability of phosphates in the soil is affected by the presence of combined silica and an excess of calcium oxide over that required for tricalcium phosphate. Agrochemical experiments showed that the best fertilizing effect is possessed by phosphates which least readily pass into hydroxyapatite. The work is being carried out by V. V. Illarionov, R. E. Remen, A. V. Sokolov, T. D. Koritskaya, and others. Investigations on the mechanism of the hydrothermal process of treating apatite were carried out by N. N. Postnikov and A. A. Ionass in the thermal laboratory and by V. V. Illarionov and R. E. Remen in the NIUIF laboratory, which is directed by the author.

Study of the hydrothermal process established the effect of traces of various substances, particularly SiO_2 , Al_2O_3 , and Fe_2O_3 , on the degree of defluorination and the passage of phosphate into the citrate-soluble form. Preliminary experiments established the effect of small amounts of salts of alkali and alkaline-earth metals, and also of silica and aluminum and ferric oxides, on the polymerization of metaphosphoric acid and its salts, and this knowledge made it possible to obtain the latter in different degrees of solubility or mobility in the soil (Zh. V. Kirillina, T. A. Banskchikova, and others). At the same time we started a more profound investigation of the polymerization of P_2O_5 and HPO_3 .

In our examination of the possible ways of improving the manufacture of fertilizers, we did not confine ourselves to phosphate and complex fertilizers, but also sought ways of improving the technology of nitrogenous and potash fertilizers. Over a period of years we have given much attention to the problem of directed modification of the crystal structure of ammonium nitrate.

The processes of crystallization of ammonium nitrate have long attracted the attention of technologists, crystallographers, and physical chemists: on the one hand, because of its richness in crystalline forms and transformations under readily accessible physicochemical conditions, which is of great interest from the point of view of method and of theory, and, on the other hand, because of the enormous importance of this salt as an excellent nitrogenous fertilizer and as a component of explosives. We have often pointed out that investigators in the field of the technology of mineral salts make insufficient use of modern concepts of the physics of solids and crystal chemistry, particularly the energy and kinetic approaches; they make too little use also of the large arsenal of methods in metallography, which has been so fruitful in the development of modern metallurgy.

The methods of quenching, tempering, annealing, modifying and other physicochemical processes used in the metallurgical industries have until recently received no extensive application in the manufacture of salts, although the processes of crystallization, recrystallization, and the preparation of salts in a definite crystalline modification and in crystals of definite size are in many ways analogous. The main objects of our investigation were ammonium nitrates, though some experiments were carried out also with potassium, calcium, and other nitrates. Apart from the five known and generally recognized crystalline modifications of ammonium nitrate having transition temperatures of -16° , $+32.5^\circ$, $+84.5^\circ$, and $+125^\circ$, there is still another modification (metastable; about 50°), which we investigated by methods of crystal optics, thermography, and x-ray analysis. Apart from the two further known modifications obtained at pressures of about 1.5 and 2.7 atm, S. M. Rubinchik and the author investigated the polymorphous transformations down to -196° , for which purpose we used the universal cooling-heating microscope stage designed by Tsurinov and Volnova in the Institute of General and

Inorganic Chemistry. We used liquid nitrogen as cooling agent. The process was filmed in color through the microscope in polarized light. This work established the existence of a low-temperature modification of ammonium nitrate below -170° , and we called it Modification VII. With the aid of a microscope fitted with a cooling-heating object stage, and also with the aid of thermographic and, to some extent, x-ray analysis, we succeeded in studying the favorable effect of quenching on the preparation of Modification III. We showed that ammonium nitrate quenched at -20° consists essentially of Modifications V and VI, and that ammonium nitrate quenched at -196° consists of Modifications IV and VII. Some of the results of these investigations were published in the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences, 1954, page 209.*

Some preliminary experiments were carried out on the reduction of the caking of ammonium nitrate by the introduction of traces of surface-active agents; this work is of practical interest and requires development. These investigations were carried out by the author in conjunction with T. V. Glazova and S. M. Rubinchik in the Laboratory of Scientific and Applied Photography and Cinematography of the Academy of Sciences of the USSR by means of microcinematography.

In working on the solution of industrial problems, chemical technologists have to expend considerable time and effort on the verification and assimilation of the results of laboratory investigations on the larger pilot-plant and factory laboratory scales. In this connection we have undertaken a study of "the methodological basis of experimental work in chemical technology", which, however, is not fully in keeping with the subject of the present paper and deserves separate treatment.

SUMMARY

From this review of exploratory work we can 1) decide to some extent which results of the exploratory work deserve further development and utilization, and 2) arrive at some general views concerning the development of the exploratory investigations.

1. Subjects that require further development and later, possibly, exploitation under manufacturing conditions include: thermal dissociation of calcium phosphates with formation of P_2O_5 ; defluorination of phosphates in a fluid bed with natural gas; the process of fusing Kara-Tau phosphorites without use of steam; the preparation of ammonium and potassium metaphosphates of various solubilities; the preparation of ammonium magnesium phosphate monohydrate; the absorption of hydrogen fluoride by solid absorbents such as limestone and nepheline. The theoretical investigations that must be more extensively and thoroughly developed include:

- a) study of the relation between the agronomic effectiveness of various phosphate compounds and their compositions and structures (with the use of radioactive P and Ca isotopes);
- b) investigation of the physicochemical conditions for the polymerization of P_2O_5 and metaphosphates and development of methods for determining the degree of polymerization.

2. The development of exploratory investigations is an important and absorbing task. The important task of the supervisors and teachers is to instill the taste for pioneering, creative, exploratory work.

In science and technology, as in all manifestations of life, we find an enormous diversity: in some cases we have conception, growth, blossoming, and the bearing of fruit, in others we have a thought, scarcely conceived when it fades and perishes, and in still others, after a prolonged latent period, a latent idea unexpectedly begins to develop vigorously. Raw materials, methods, processes, and theories are all in a state of perpetual movement. The experimental and supervisory workers in science and technology must give much careful attention to the embryonic stage of the formation of new ideas and suggestions; their keen sight must be able to spot "points of growth". We must advance more boldly and with more initiative.

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A. N. BAKH'S WORK IN CHEMISTRY, AND HIS ROLE IN
THE DEVELOPMENT OF SOVIET PHYSICAL CHEMISTRY

A. N. Frumkin

(Paper read at meeting held in celebration of the centenary of the birth
of A. N. Bakh, March 18, 1957)

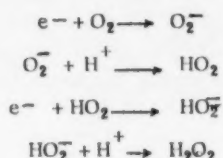
The subject matter of my paper is somewhat more restricted than its title would suggest. My main object is to trace the influence of A. N. Bakh's concepts of the mechanism of oxidation processes on the development of physicochemical investigations in this field and to compare his views with the results obtained more recently.

Bakh's first main postulate - which he stated sixty years ago [1] simultaneously with the German chemist Engler - was that an oxygen molecule O_2 does not immediately split into atoms when it enters into a chemical reaction. In the initial stages of its transformation these atoms remain linked though a single valence. It follows that the primary oxidation products should be peroxides. This conclusion, however, is still inadequate for the explanation of the phenomena observed. The formation of peroxides in oxidation reactions is often accompanied by the oxidation of other substances, which would not themselves react with oxygen under the given conditions. For example, according to Hoppe-Seyler [2], oxidation of the hydrogen of "palladium hydride" by molecular oxygen may be accompanied by vigorous oxidation reactions, indigo being converted into isatin, benzene into phenol, etc. These phenomena cannot be explained by the action of hydrogen peroxide - the final product of the oxidation of the atomic hydrogen present in the palladium - because hydrogen peroxide is not a sufficiently powerful oxidizing agent and does not undergo the reactions described. Bakh therefore proposed that, when oxidized, "atomic hydrogen can give not only hydrogen peroxide, but also still higher peroxides". This quotation from Bakh's classical paper is almost verbatim, but the terminology has been somewhat modernized: Bakh speaks not of atomic hydrogen, but of "hydrogen at the moment of its liberation", and he refers to H_2O_2 as "hydrogen dioxide", which is no longer in accord with usage.

Bakh's concepts, therefore, can be summed up in two main theses: 1) in the attachment of an oxygen molecule to a molecule of the substance undergoing oxidation, a linkage between the O atoms is preserved; and 2) the primary oxidation product is a "higher" peroxide, which differs from the usual stable peroxides. Bakh considered that the higher peroxide of hydrogen was H_2O_4 , consisting of a chain of four oxygen atoms with a hydrogen atom at each end. I shall return later to the question of the structure of the higher peroxide of hydrogen; at the moment I wish to indicate how the two main theses of A. N. Bakh became modified in the subsequent period.

Among the autoxidation processes examined closely by Bakh in his early investigations, the oxidation of metals, e.g., zinc or lead, by atmospheric oxygen in presence of water with simultaneous formation of hydrogen peroxide was of great importance from the point of view of reaction mechanism. We now know that in these reactions the principal role of the metal is that of electron donor: metal atoms, by losing electrons which attach themselves to oxygen, are transformed into the corresponding ions. The reaction addition of electrons to O_2 can be effected in a more direct way if conditions are created under which the whole process is limited to what we may call "the oxidation of an electron". This is realized in the electroreduction of oxygen at a metal cathode; for reasons that we shall not consider here, it is best to use a mercury cathode for this purpose. As a result of numerous investigations - particularly those of Soviet electrochemists, among which V. S. Bagotsky deserves special mention - the mechanism of the electroreduction of oxygen at a mercury cathode

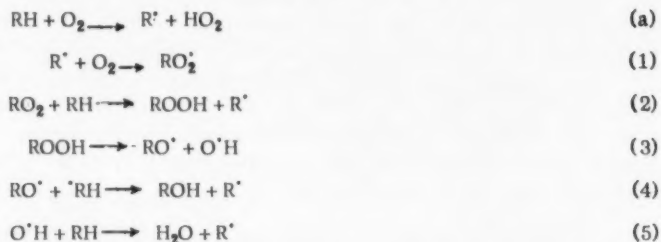
can be considered to be completely elucidated; the process can be broken down into the following stages (e^- denotes an electron):



It will be seen that the primary reaction product is the species O_2^- . This combines with a hydrogen ion to give HO_2 , i.e., into an unstable intermediate compound, the monomer of the higher peroxide of hydrogen discussed by A. N. Bakh. By accepting a second electron, HO_2 passes into the HO_2^- anion of hydrogen peroxide, which passes further into a hydrogen peroxide molecule H_2O_2 , i.e., stable products in which, however, the bond between the two oxygen atoms is preserved. At other cathodes, e.g., platinum, the electron and hydrogen ion do not appear to add to different species, but first combine to give H atoms, which give HO_2 with O_2 ; this is still near to A. N. Bakh's concepts. Rupture of the bond between the O atoms, which results in the conversion of hydrogen peroxide into water, occurs only under much more vigorous conditions, and in the electrochemical reaction is possible only when the potential of the cathode is displaced to more negative values. Hence, this simple low-temperature reaction in which an oxygen molecule takes part is precisely in accord with the scheme proposed by A. N. Bakh.

Let us now examine the reaction of molecular oxygen in oxidation processes occurring at somewhat higher temperatures, e.g., the oxidation of hydrocarbons, in which oxygen acts on substances which, unlike an electron have no free valence. Clarity was introduced into these matters by the work of N. N. Semenov and his school. Even in 1934, in his monograph "Chain Reactions" N. N. Semenov wrote: "I wish to show that our chain theory of oxidation may be regarded as the logical development of classical theories of oxidation resulting from the consideration of . . . new facts that have emerged concerning the oxidation of gases and vapors."

I give here the scheme for the oxidation of the hydrocarbon RH in the form in which it is given by N. M. Emanuel and coworkers [3], omitting a few of the details and discussing only its main features. R^\cdot here indicates a hydrocarbon residue, i.e. a free radical, and the dot denotes a free valence.



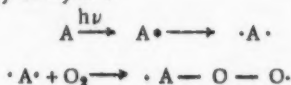
Our main interest lies in reactions (1) and (2). As a result of (1) the free radical R^\cdot combines with O_2 molecule with formation of an RO_2^\cdot radical - an analog of A. N. Bakh's higher peroxide. In the reaction (2) this higher peroxide passes into the relatively stable hydroperoxide ROOH. In these schemes something essentially new has appeared, thus vindicating Bakh's statement twenty years ago at a conference held on the occasion of the fortieth anniversary of the Bakh-Engler peroxide theory [4]: ". . . it is my hope that a new development in the peroxide theory will spring from chemical physics and provide an explanation for all the experimental facts . . .". We shall now see what this new development is. The above scheme indicates that the oxygen in reaction (1) does not add to the original hydrocarbon molecule RH, but to its scission product, the radical R^\cdot . For the reaction to go, it is essential that these active radicals should be formed in sufficient quantity. They are generated initially in the reaction (a), in which the original hydrocarbon is oxidized. This reaction, however, requires a considerable activation energy, and it rarely occurs; it is necessary only for the initiation of the chain. Subsequently, active species are provided by the chain process itself, as can be seen from reactions (2) - (5). Special significance for the kinetics of the process is to be found in stage (3), in which two active species are formed: branching of the chain occurs so that the whole process is autoaccelerating.

Here we give only the stages leading to the formation of the alcohols ROH by mechanism (4); the reaction actually goes further with formation of ketones and acids. N. M. Emanuel was able to confirm the proposed scheme with the aid of some shrewd experiments; in particular, it was found that the rate at which the final reaction products accumulated bore a simple relationship to the concentration of peroxides at each moment of the process. The important point for us is that in the interpretation not only of the mechanism, but also of the kinetics of oxidation reactions of hydrocarbons on the basis of Semenov's chain theory, all the essential principles underlying Bakh's views were preserved. This enabled the authors of the papers that I have cited to conclude that "A. N. Bakh's peroxide theory still, at this present time, is the operative theory for the explanation of the kinetics and chemistry of the oxidation of hydrocarbons."

Active species arising by the decomposition of a peroxide [reaction (3) in the scheme given above] ensure the continuation of the oxidation reaction. However, if a sufficiently unsaturated, e.g., dienic, hydrocarbon is oxidized, these active species may act as initiators also for polymerization reactions. As a result, there is a close relationship between oxidation and polymerization reactions, a relationship that has been elucidated as a result of many years of investigation by S. S. Medvedev and his coworkers and can be understood only when the part played by the intermediately formed peroxy compounds is taken into account.

Chain theory has greatly extended the scope of the possible application of A. N. Bakh's concepts in the interpretation of oxidation processes. However, as Bakh himself emphasized, the formation of unstable and stable peroxides can occur and have a decisive significance also in the case of oxidation processes which do not have a chain character. This occurs, for example, in the formation of triphenylmethyl peroxide, which was discussed frequently by Bakh and which probably proceeds by a scheme analogous to that cited at the beginning of this paper. As Frumkin and Burshtein [5] have shown, short-lived peroxide forms arise also in the simple process of absorption of oxygen on the surface of activated carbon.

Up to now we have considered the part played by peroxides in oxidation reactions in which the process is possible as a result of the utilization of the energy of an electric field or of the thermal motion of the molecules. An important group of oxidation processes is formed by processes proceeding under the action of light, the mechanism of which has been the subject of particularly profound study in our country by A. N. Terenin and his students. In this case also, the ideas of A. N. Bakh on the parts played by active peroxy compounds and the ways in which they may be formed were frequently applied and simultaneously acquired new formulations. By way of example I will refer to one of the numerous schemes of photooxidation reactions given in Terenin's book "Photochemistry of Dyes":



In absorbing a light quantum, the molecule of the aromatic compound A passes into the excited state A^* and further, by electronic rearrangement, into a diradical with two free valences $\cdot A \cdot$. This last species combines with an oxygen molecule and gives the unstable peroxide $\cdot A - O - O \cdot$, which by collision with another A molecule can give up its excess of energy and pass into the chemically isolable peroxide AO_2 or initiate a chain oxidation reaction.

The above discussion indicates the significance of the suggested existence of higher peroxy compounds for the interpretation of the mechanism of oxidation reactions on the basis of A. N. Bakh's theory. The simplest member of this class of compounds is the monomeric form of the higher peroxide of hydrogen HO_2 , which is formed as an intermediate product in solution or in the gas phase in various oxidation reactions. Special importance has recently been acquired by the theory of intermediate HO_2 formation in the interpretation of processes occurring in aqueous media under the action of ionizing radiations. The substance HO_2 has not yet been isolated in the individual state, and it probably cannot be isolated because of its instability. However, x-ray structure analysis has shown that the higher oxides — the so-called superoxides — of the alkali metals, which have the chemical composition of MO_2 and are quite stable in the solid crystalline state, contain O_2^- ions in their lattices, these being the ions that I have already mentioned in connection with the mechanism of the electroreduction of oxygen. These oxides, therefore, must be regarded as salts derived from the unstable peroxide HO_2 . For our information on this important and interesting group of compounds we are indebted mainly to I. A. Kazarnovsky, whose profound investigations (carried out in part in collaboration with J. D. Bernal) made a considerable contribution to the elucidation of the structures of crystalline

peroxides and superoxides. By synthesis under high pressure, I. A. Kazarnovsky and G. P. Nikolsky have obtained a new important member of this class — sodium superoxide NaO_2 — which has been found to be a valuable air-regeneration agent. More recently, I. A. Karnovsky has succeeded in obtaining even more highly oxidized products of the type of potassium ozonide KO_3 , whose interesting properties, however, I cannot discuss here.

As already stated, A. N. Bakh suggested that two unsaturated HO_2 radicals combine with formation of a molecule of hydrogen tetroxide H_2O_4 , and he attempted to confirm this suggestion by various experimental results. Thus, in the decomposition of KO_2 with dilute sulfuric acid with efficient cooling, Bakh obtained a solution which in permanganate titration yielded much more oxygen than would be expected for a solution of ordinary hydrogen peroxide. Bakh considered that this solution contained the hypothetical tetroxide H_2O_4 [6]. Various analogous suggestions were made also by later investigators, but no unequivocal proof of the existence of aqueous H_2O_4 solutions of appreciable concentration and stable at ordinary temperatures has yet been obtained. The nearest approach to the solution of the problem of the preparation of H_2O_4 is probably that of Kobozov, Nekrasov, and Eremin [7], whose work was published at the end of last year. Further information about the method was communicated quite recently in a paper by I. I. Skorokhodov read in the Chemistry Department of the Moscow State University. The authors bombarded a film of liquid ozone at -195° with atomic hydrogen. The blue color disappeared and a glassy substance was obtained which decomposed when heated to -55° with liberation of oxygen and formation of an aqueous solution of hydrogen peroxide. For each mole of H_2O_2 formed, one mole of oxygen was liberated, which indicates that the original substance was very probably of the composition H_2O_4 . In the author's opinion, under other conditions of formation of such "glassy substances", they may contain frozen monomer — the free radical HO_2 .

Oxidation reactions of organic compounds with atmospheric oxygen lie at the basis of processes for the preparation of synthetic fats, acetic anhydride, and other valuable products; they occur spontaneously in the fading of dyes. We meet these same reactions in the working of the gasoline engine of an automobile or aircraft. The correct understanding of the mechanism of oxidation processes, and in particular of the part played by peroxides in these processes, is therefore of great importance for the improvement of the conditions under which important technological processes occur, and it can result in the discovery of new ways of bringing these processes about, as is clear from N. M. Emanuel's recent work.* An interesting example of a technological process in which valuable products are obtained through the intermediate formation of a peroxide is the preparation of phenol and acetone by the decomposition of "cumene hydroperoxide", which is prepared by air-oxidation of cumene. In describing this method, B. D. Kruzhalov and P. G. Sergeev justifiably state that the process proceeds "in complete accord with the autoxidation theory advanced more than fifty years ago by A. N. Bakh" [9].

I have attempted to give a brief characterization of the development of ideas on the mechanism of reactions in which oxygen part — the essence of the peroxide theory of oxidation as applied in modern chemical kinetics, inorganic chemistry, and chemical technology. In so doing, without, I consider giving any unfair treatment, I have referred mainly to the work of Soviet investigators. Such concentration of these investigations in our country is not, of course, an accident, but a direct reflection of the enormous influence of A. N. Bakh on the development of Soviet chemistry.

Bakh's role as an initiator of physicochemical investigations was also very great. The L. Ya. Karpov Chemical Institute, which was originally the Central Chemical Laboratory of the Supreme Council of the National Economy and was founded jointly by A. N. Bakh and L. Ya. Karpov in 1918, is the largest (and for some years the only) center for physical chemistry in our country. The investigations of the Karpov Institute have made important contributions to such important branches of physical chemistry as the structure of matter, the physical chemistry of polymers, kinetics and catalysis, electrochemistry, theory of solutions, surface phenomena, radiation chemistry, and theory of the solid state, contributions of such significance that would be difficult to overestimate them. Various problems of great practical importance have been solved in the Karpov Institute, and this has helped greatly in the development of our chemical industry and in the strengthening of the defenses of our Fatherland.

A. N. Bakh possessed in high degree the ability to attract youth and to kindle and maintain its enthusiasm. From the very start of the activities of the Karpov Institute, he built up a group of young physical chemists who

*A review of the present position of the question of the structure and properties of organic peroxides has been given by A. Rieche [8].

later had considerable influence on various branches of this science. He very easily and rapidly oriented his ideas, even in branches of knowledge that were remote to him. With an approach that was just as kind as it was correct, he was able to appreciate the significance and future prospects of various lines of work, which enabled him to render friendly assistance not only to the young scientists who had the good fortune to work with him in the Karpov Institute, but also to many others, now famous Soviet chemists.

In conclusion, in the name of the generation of Soviet physical chemists that stepped into the scientific arena shortly after the October Revolution and to which I myself belong, I should like to make a grateful tribute to this great man and great scientist.

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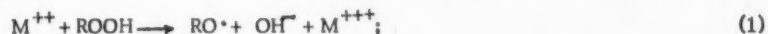
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INITIATION OF THE OXIDATION OF 2,7-DIMETHLOCTANE BY FREE RADICALS GENERATED BY THE PHOTOLYSIS OF SALTS OF METALS OF VARIABLE VALENCE

I. Ya, Shlyapintokh and N. M. Emanuel

It is known that the oxidation of hydrocarbons by molecular oxygen proceeds by a chain mechanism with degenerate branching [1]. In liquid phase oxidation there is usually a considerable period of induction associated with the low rate of formation of active centers w_0 . The value of w_0 itself is often determined by the rate of the process in the initial stage of reaction when there is still very little of the products that give degenerate branching. Hence, the action of chemical and physical agents that increase w_0 should result in increase in the rate of the oxidation process [2].

It has been shown in various investigations that the period of induction may be considerably shortened by the introduction of salts of metals of variable valence into the system [3-5]; In this connection it has generally been assumed that the catalytic effect produced by additions of salts is to be explained by their reactions with components of the system with formation of free radicals. In the schemes most commonly suggested it is assumed that free radicals are formed as a result of reaction of cations of a metal M of variable valence with peroxides:



Reactions proceeding in accordance with schemes (1) and (2) can occur in aqueous solutions, in which there is a large gain of energy due to the formation of hydrated OH^- and H_3O^+ ions. In nonionizing solvents, and in hydrocarbons in particular, the initiation of oxidation processes must proceed in an essentially different way without the formation of ions: •



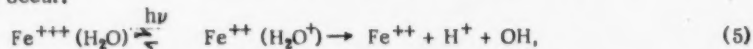
in which X is an acid residue. However, as will be seen from this scheme, in nonionizing solvents initiation again consists in the formation of free radicals. It would be expected, therefore, that the rate of an oxidation reaction catalyzed by salts of variable valence could be increased still more if the system could be treated in some way that would produce more free radicals.

For the generation of free radicals in solutions, photochemical electron-transfer reactions have recently been used [6-9]. These reactions, which are characteristic for molecules containing ionic bonds, constitute one of the forms of photolysis reactions. In a photochemical electron-transfer reaction, the excitation and subsequent breakdown of ionic molecules are accompanied by intramolecular electron transfer from one part of the molecule to another.

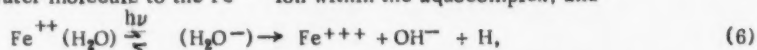
Reactions of this type have generally been observed and studied in the liquid phase in polar solvents, generally water. In polar solvents, ions are usually strongly solvated. In the transfer of an ion from the gas

†Reactions (3) and (4) for the initiation of oxidation processes in nonionizing solvents were proposed by D. G. Knorre.

phase into the liquid, there is usually a considerable change in electron levels, and new levels arise, thus indicating the strong interaction between the ion and solvent molecules. On this basis it may be considered that solvate complexes are formed in the dissolution of ions. The excitation of these solvate complexes may lead to their breakdown either with the transfer of an electron from the central ion to the solvate envelope or with electron transfer in the opposite direction. The first process is characteristic for reduced forms of cations and for anions, and the second — for oxidized forms of cations. For example, in an aqueous solution of iron salts the following processes may occur:



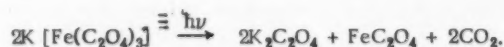
i.e., electron transfer from the water molecule to the Fe^{+++} ion within the aquocomplex, and



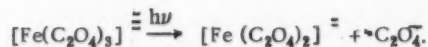
i.e., intramolecular transfer of an electron from the central Fe^{++} ion to one of the ligands. We see that in reactions (5) and (6) a change occurs in the valence state of the central ion, and an OH radical (5) or H atom (6) is formed. The formation of an OH radical and Fe^{++} in (5) and of an H atom and Fe^{+++} in (6) was proved by analyses for Fe^{++} and Fe^{+++} and by the liberation of oxygen and hydrogen, respectively [10, 11]. H atoms and OH radicals obtained in photochemical electron-transfer reactions have been used for the initiation of polymerization reactions [12].

These photochemical processes occur not only in solvate complexes, but also in other complex compounds. Excitation of a complex anion or cation often leads to a photoreaction in which a free radical is formed and the valence of the central ion is changed. If the bonds in the complex are regarded as ionic, then such a process can be considered as an electron-transfer process.

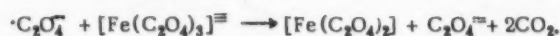
Thus, in the irradiation of a solution of the complex potassium ferric oxalate, the following reaction occurs [13]:



This reaction appears to consist of two stages. In the first stage photochemical electron transfer occurs from the $\text{C}_2\text{O}_4^{\equiv}$ ion to Fe^{+++} :



This process results in the formation of the radical ion $\cdot\text{C}_2\text{O}_4^-$, and the valence of iron is lowered. In the second stage $\cdot\text{C}_2\text{O}_4^-$ reacts with the original ion:



Photochemical electron-transfer reactions can be brought about not only in the liquid phase, but also in the vapor phase; it can also be brought about in nonpolar solvents. The simplest example of reaction of this type is the photodecomposition of a diatomic ionic molecule A^+B^- into its atoms in the normal or excited states:



In reaction (7) transfer of an electron from B to A occurs. Reactions of type (7) are observed also in the photolysis of molecules of more complicated structure. It will be clear from the last example that the treatment of photochemical electron-transfer reactions as a special type of reactions is very arbitrary and that in practice there is no sharp boundary between photochemical electron-transfer reactions and photodecomposition into atoms and radicals. In fact, if the molecule AB is purely covalent, its photodecomposition according to equation (7) is simple dissociation and is not associated with the transfer of an electron. In all intermediate cases, in which the bond in the molecule is neither purely ionic nor purely homopolar, the photodecomposition of the molecule $\text{A}^{+\delta}\text{B}^{-\delta}$ in accordance with (7) may be treated both as a photochemical electron-transfer reaction and as a photodissociation reaction depending on which of the types of bond is predominant.

With the object of applying photochemical methods in the study of the mechanism of the oxidation of hydrocarbons, we carried out work on the photoinitiation of the oxidation of 2,7-dimethyloctane. As photoinitiators we selected salts of metals of variable valence — ferric and cupric stearates. In hydrocarbon solution these salts were in the nonionized, molecular form. By analogy with the photolysis reactions of halides [14]

and of complex ions we considered that the photolysis of stearate molecules would proceed with transfer of an electron from the acid residue to the metal. As a result of this reaction $\text{Cu}^{(1)}$ and $\text{Fe}^{(2)}$, respectively, should be formed together with free $\text{C}_{18}\text{H}_{35}\text{O}_2^\cdot$ radicals. Radicals of this type were obtained, for example, by Farcas and Wansbrough-Jones in the photolysis of aqueous acetate, propionate, and butyrate solutions [15] and by Razuvaev in the thermal decomposition of acetyl benzoyl peroxide [16]. It was shown in these investigations that the main reaction undergone by RCO_2^\cdot radicals (R = aliphatic radical) is their breakdown into the hydrocarbon radical R^\cdot and CO_2 . It may be supposed, therefore, that the photolysis of $\text{Cu}^{(2)}$ and $\text{Fe}^{(3)}$ stearates will result in the formation of $\text{Cu}^{(1)}$, $\text{Fe}^{(2)}$, CO_2 , and hydrocarbon radicals $\cdot\text{C}_{17}\text{H}_{35}$.

EXPERIMENTAL

2,7-Dimethyloctane was prepared from isopentyl bromide by the Wurtz reaction. The product was heated for six hours with 10% alcoholic sodium hydroxide to hydrolyze unchanged isopentyl bromide, and was then washed with water and shaken in a separating funnel with 15% oleum. The 2,7-dimethyloctane was then freed from peroxides by shaking it with sodium metabisulfite. It was washed repeatedly with water, dried over calcium chloride, and distilled in a glass apparatus at a residual pressure of 15 mm. The purity of the product was checked spectrophotometrically by its absorption in the ultraviolet. Ferric and cupric stearates were prepared by mixing sodium stearate ("pure for analysis" grade) solutions with solutions of salts of the corresponding metals ("chemically pure" grade). The precipitates of stearates were washed with water on the filter and dried in a vacuum at 70° to constant weight.

The dark reaction was carried out by passing oxygen through a layer of 2,7-dimethyloctane in an oxidation cell of the design described in [5]. The photochemical reaction was carried out in the oxidation cell shown diagrammatically in Fig. 1. The source of light was an SVDSH-250 lamp. The light from the lamp was reflected from an aluminized mirror and passed to the cell, which was contained in a thermostat. Light passed into the cell through the quartz window 1, sealed to the upper part of the ground joint. During the reaction test samples were taken periodically from the vessels through the tube 2 in order to follow the kinetics of formation of acids.

The kinetic curves obtained in dark and photochemical experiments with $\text{Cu}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$ and $\text{Fe}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$ catalysts at 123° are given in Figures 2 and 3, from which it will be seen that the formation of acids occurs more rapidly in the photochemical reaction than in the dark reaction.

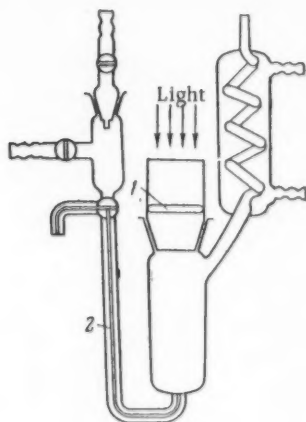


Fig. 1. Oxidation cell for the photochemical experiments.

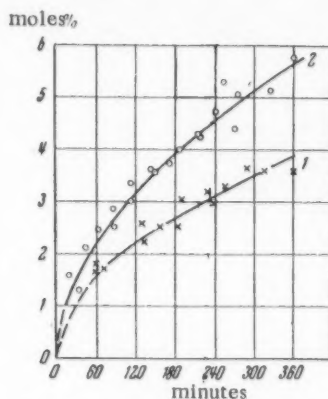


Fig. 2. Kinetic curves for the formation of acids in dark (1) and photochemical (2) experiments. Catalyst $\text{Cu}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$, temperature 123° .

In order to determine the mechanism of the photochemical initiation of the oxidation process, we carried out the photolysis of ferric stearate as a solution in 2,7-dimethyloctane in an atmosphere of nitrogen. After irradiation for 4-5 hours a sample was taken and tested for ferrous iron. The sample was taken in a test

tube through which nitrogen was being passed, 0.5, ml of 5 N HCl was added, and the mixture was heated to 100° with continuous bubbling of nitrogen. As a result, much of the salt passed into the hydrochloric acid solution. The mixture was cooled to room temperature in an atmosphere of nitrogen, the 2,7-dimethyloctane layer was separated, the hydrochloric acid extract was neutralized, and a crystal of 2,2'-bipyridine. In experiments on irradiation in an atmosphere of nitrogen, a distinct test for ferrous iron was obtained, but in control experiments, in which the solution of ferric stearate in the hydrocarbon was heated in the dark for 4-5 hours in an atmosphere of nitrogen, no ferrous iron was detected. Hence, absorption of light resulted in change in the valence state of iron from ferric to ferrous.

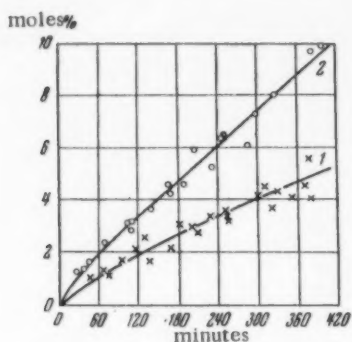


Fig. 3. Kinetic curves for the formation of acids in dark (1) and photochemical (2) experiments. Catalyst $\text{Fe}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$; temperature 123°

As already stated in the introduction, we supposed that in the photolysis of $\text{Fe}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$, formation of $\text{Fe}^{(2)}$ would be accompanied by formation of the radical $\text{C}_{18}\text{H}_{35}\dot{\text{O}}_2$. If this is so then it should be possible to observe the liberation of CO_2 in the irradiation of a solution of $\text{Fe}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$ in an atmosphere of nitrogen. When analyzing for CO_2 , we carefully purified the original nitrogen from this gas and blew the nitrogen through the oxidation cell at 123°. The gas then passed to a trap cooled to -60° and further to an absorber containing alkali. The experiments showed that the liberation of CO_2 did indeed occur in the photolysis of $\text{Fe}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$ in an atmosphere of nitrogen. The amount of gas liberated was found to be very small: the amount of carbon dioxide liberated in two hours was equivalent to only 0.05 ml of 0.1 N NaOH. In the corresponding dark control experiments, in which nitrogen was passed through a solution of $\text{Fe}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$ in 2,7-dimethyloctane at the same temperature, no liberation of carbon dioxide occurred.

Hence, the catalytic effect produced by irradiation is associated with the photolysis of the salt of a metal of variable valence into the reduced cation and the radical $\text{C}_{18}\text{H}_{35}\dot{\text{O}}_2$, which decomposes into the hydrocarbon radical $\cdot\text{C}_{17}\text{H}_{35}$ and CO_2 . The photochemical acceleration of reaction is probably to be explained by reactions of both the hydrocarbon radical $\cdot\text{C}_{17}\text{H}_{35}$ and the ferrous salt with peroxides formed in the course of the oxidation process.

From the amount of carbon dioxide liberated during the irradiation and from the difference between the amounts of acids formed during the same time in photochemical and dark oxidation we made an estimate of the average length of chain \bar{n} in the oxidation reaction of 2,7-dimethyloctane. It was found that $\bar{n} = 300$. This estimate is undoubtedly too high, because initiation of oxidation can occur also on account of reaction of ferrous salt with the radical $\text{C}_{18}\text{H}_{35}\dot{\text{O}}_2$, and this reaction was not taken into consideration in the calculation of the length of chain.

SUMMARY

1. It was shown that the photolysis of cupric and ferric stearates in 2,7-dimethyloctane at elevated temperature (123°) in presence of molecular oxygen accelerates the oxidation of the hydrocarbon.
2. Photolysis of $\text{Fe}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$ results in the formation of $\text{Fe}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$ and the free radical $\text{C}_{18}\text{H}_{35}\dot{\text{O}}_2$, which was detected by the liberation of CO_2 when photolysis of the salt occurred in an atmosphere of nitrogen.
3. The catalytic effect produced by the photolysis reaction is to be explained by reactions both of the $\cdot\text{C}_{17}\text{H}_{35}$ radical formed by decomposition of the $\text{C}_{18}\text{H}_{35}\dot{\text{O}}_2$ radical and also of a ferrous salt with peroxy compounds.
4. It was estimated that the effective length of chain in the oxidation process was $\bar{n} \leq 300$.

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EFFECT OF THE MOLECULAR STRUCTURE OF AN ALCOHOL ON THE KINETICS OF ITS DEHYDROGENATION

COMMUNICATION 1. C₂ AND C₃ ALCOHOLS

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This investigation had the object of obtaining data on the selectivity of a catalyst and on the relation between its activity and the structure of the molecules being transformed. In previous work on the dehydrogenation of hydrocarbons over a mixed oxide catalyst, we showed that the selectivity of the catalyst depends on the structure of the original hydrocarbon. It was, for example, found that over a given catalyst the rate of dehydrogenation of an olefin is much higher than for a saturated hydrocarbon having the same number of carbon atoms in the molecule. The rate of dehydrogenation of aliphatic-aromatic hydrocarbons is still higher than that of olefins, and isopropylbenzene, with its branched chain, is dehydrogenated more rapidly than ethylbenzene.

It was of interest to investigate the effect of molecular structure on the rate of catalytic dehydrogenation for substances of other types over the same catalyst. For this purpose we took alcohols of various structure. As is well known, the kinetics of the dehydrogenation of saturated alcohols from ethyl to isopentyl have been investigated over copper [1,2]. There are no references in the literature to work on the effect of the structure of an alcohol on the kinetics of its dehydrogenation over other catalysts.

The present paper describes work on the kinetics of the dehydrogenation of ethyl, propyl, allyl, and isopropyl alcohols over an oxide catalyst. Determinations were made of the relative adsorption coefficients of the reaction products, the rate constants of the reactions over a wide temperature range, the true activation energies of the dehydrogenation reactions, and the free energy, enthalpy, and entropy changes in adsorptional displacement at catalytically active centers during the dehydrogenation of alcohols.

EXPERIMENTAL

The experiments were carried out by the flow method in the same apparatus as that used for hydrocarbons [3], though some modification was made for the feed of liquid. The alcohol was fed by an automatic arrangement which ensured constant rate of passage. The catalyst was contained in a quartz tube, diameter 16 mm, and was supported on a quartz grid sealed at a 6-mm constriction in the tube at the point where the reaction products left the catalyst. A pocket for a thermocouple was sealed in at the other end of the tube, and its upper end was about 5 cm above the grid. The quartz tube was heated in an electric furnace provided with an electronic thermoregulator. The temperature was read on a millivoltmeter connected to a nichrome-constantan thermocouple.

Before the experiments the alcohols were dried over potassium carbonate and distilled through a 60-plate column. In the distillation, a fraction boiling within a range of 1° was collected (Table 1). The ethyl alcohol used was not rendered absolute. Aldehydes and ketones for experiments on the rates of dehydrogenation of binary mixtures of alcohol and reaction product were obtained by fractionation from catalyzates obtained from special prolonged experiments on the dehydrogenation of alcohols over the same catalyst. The physical constants [4, 5] of the starting materials are given in Table 1.

All experiments were carried out with the same weight (11 g) of oxide catalyst. It should be noted that

TABLE 1

Physical Constants of Starting Materials

Substance	Experimental values			Data from literature [4, 5]		
	B.p. (°C)	d_4^{20}	n_D^{20}	B.p. (°C)	d_4^{20}	n_D^{20}
Ethyl alcohol	78.1	0.7980	—	78.4	0.789	1.3619
Propyl alcohol	97-97.2	0.8044	1.3858	97.8	0.804	1.38543
Allyl alcohol	96.7	0.8537	1.4132	96.6	0.854	1.41345
Isopropyl alcohol	82.1-82.4	0.7887	1.3774	82.5	0.789	1.37757
Acetaldehyde	21.0	0.7839	—	20.8	0.783	—
Propionaldehyde	49.1	0.8078	1.3636	49.5	0.807	1.36356
Acrolein	52.5-53	0.8387	—	52.5	0.840	1.4022(19.5°)
Acetone	56.5	0.7924	1.3593	56.5	0.792	1.3590

experiments on the dehydrogenation of hydrocarbons had been carried out on this sample of catalyst over a period of one year, and the catalyst still preserved its original activity. In the experiments with alcohols the activity of the catalyst remained constant, as judged by the reproducibility of results for the dehydrogenation of isopropyl alcohol, which was taken as a standard.

TABLE 2

Calculation of Relative Absorption Coefficients of Hydrogen

Composition of mixture (moles %)		Temperature (°C)	m_0	m	z_3
Alcohol	Hydrogen				
Propyl alcohol					
100	—	293	26	27	0.0
80	20	293	—	27	0.0
100	—	342	60	—	—
80	20	342	—	62	0.0
100	—	386	128	—	—
80	20	386	—	129	0.0
Isopropyl alcohol					
100	—	271	26	—	—
50	50	271	—	25	0.04
100	—	292	76	—	—
50	50	292	—	77	0.00
100	—	312	107	—	—
50	50	312	—	109	0.00

The liquid reaction products (catalyzate), on leaving the furnace, were collected in a receiver fitted with reflux condenser, and the readily volatile products were collected in a trap cooled by a mixture of carbon dioxide and acetone contained in a Dewar vessel. Gaseous reaction products were collected in a gas holder over saturated brine. The volume of the gas was measured accurately within 2 ml every five minutes; it was reduced to STP. The gas was analyzed for carbon dioxide content by absorption with potassium hydroxide solution, for unsaturated hydrocarbons by absorption with a solution of mercuric sulfate in sulfuric acid, and for hydrogen and saturated hydrocarbons by combustion over cupric oxide. No carbon monoxide or saturated hydrocarbons were detected in the gas. Aldehydes were determined in the liquid catalyzate with the aid of hydroxylamine hydrochloride and titration with alkali in presence of Bromothymol blue [6]. Acetone was determined by Messinger's iodometric method [7]. No appreciable amount of by-products was found in any of the catalyzates.

Before an experiment the apparatus was flushed out with nitrogen to displace air. Five minutes was allowed for the establishment of a stationary state, and only after this period were measurements on the reaction products commenced. During the experiment gas was liberated uniformly at constant rate, as can be seen from Fig. 1. The rate of reaction was determined from the volume of hydrogen evolved.

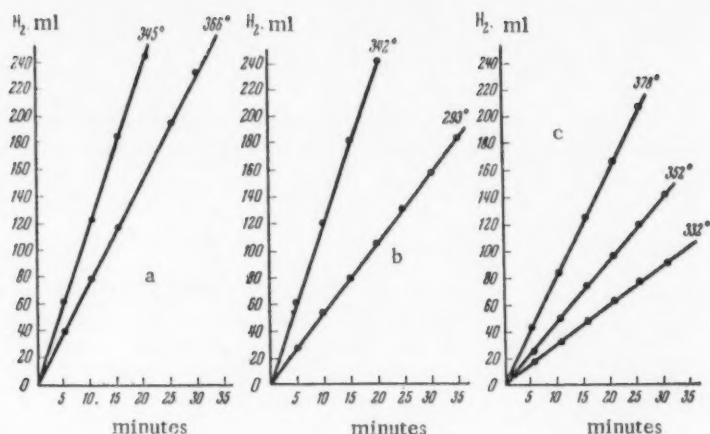


Fig. 1. Rate of gas evolution with alcohol feed of 1.05 ml in five minutes:
a) ethyl alcohol; b) propyl alcohol; c) allyl alcohol.

The experiments with alcohols showed that the catalyst was highly selective and promoted dehydrogenation almost exclusively: dehydration of the alcohols was almost or entirely absent, as is indicated by the low and in fact negligible, content of unsaturated hydrocarbons in the gas. There was a close correlation between the amount of hydrogen liberated and the amount of aldehyde or ketone obtained. After each experiment air was passed through the catalyst. The experiments with alcohols were carried out over a wide range of temperatures and with different rates of passage. The results for the different alcohols are presented in Tables 3-6.

For the determination of the relative adsorption coefficients of the reaction products, dehydrogenation rates were investigated for binary mixtures of alcohol + aldehyde or ketone and of alcohol + hydrogen at the same temperature and rate of passage as in the experiments with the pure substance. The mixtures investigated contained 25 and 50 moles % of aldehyde or ketone in the case of alcohol + aldehyde or ketone and 20 and 50% of hydrogen in the case of alcohol + hydrogen mixtures. In the latter mixtures electrolytic hydrogen was used. It was found that the relative adsorption coefficient of hydrogen on this catalyst was zero, for the reaction rate in the dehydrogenation of binary mixtures of alcohol and hydrogen was the same as for the pure alcohol (Table 2).

TABLE 3

Dehydrogenation of Ethyl Alcohol

Experiment No.	Temperature (°C)	Amount of H ₂ from 1 ml of alcohol (ml at STP)	Degree of dehydrogenation from amount of H ₂ (%)	Analysis of gas (% by volume)		
				CO ₂	Unsaturated hydrocarbons	H ₂
Alcohol feed of 1 ml in 5 minutes; theoretical amount of H ₂ from 1 ml of alcohol = 384 ml						
54	345	38.5	10.0	1.2	0.4	98.4
65	366	61.4	16.0	1.8	0.6	97.6
69	383	93.3	24.3		Not analyzed	
66	387	95.0	24.7	3.4	1.4	95.2
67	405	157.4	41.0	5.4	2.6	92.0
Alcohol feed of 0.8ml in 5 minutes; theoretical amount of H ₂ from 0.8 ml of alcohol = 308 ml						
12	362	59.4	19.2	3.2	1.0	95.8
10	386	94.0	30.5	5.6	2.2	92.2
Alcohol feed of 0.5 ml in 5 minutes; theoretical amount of H ₂ from 0.5 ml of alcohol = 198 ml						
5	342	33.5	17.4	2.0	0.4	97.6
6	366	57.5	29.9	3.4	0.8	95.8
7	391	90.0	47.0	6.0	2.0	92.0

The values of relative absorption coefficients z were calculated from the formula [8]:

$$z = \frac{\frac{m_0}{m} - 1}{\frac{100}{p} - 1} \quad (1)$$

in which m_0 and m are the rates of liberation of hydrogen by the pure original substance and by a mixture of $p\%$ of this with the substance for which z is being determined, the molar rates of passage being the same.

TABLE 4

Dehydrogenation of Propyl Alcohol

Alcohol feed of 1.05 ml in 5 minutes; theoretical amount of H_2 from 1.05 ml of alcohol = 314 ml

Experiment	Temperature (°C)	Amount of H_2 from 1.05 ml of alcohol (ml at STP)	Degree of dehydrogenation from amount of H_2 (%)	Analysis of gas (% by volume)		
				CO_2	unsaturated hydrocarbons	H_2
33	293	26	8.3	Not analyzed		
32	342	60	19.1	0.2	0.0	99.8
17	368	96	30.5	2.2	0.4	97.4
16	386	128	40.8	3.2	0.4	96.4
12	408	188	59.9	4.4	0.2	95.4
18	422	277	88.2	8.4	0.4	91.2
10	425	290	92.4	8.0	0.2	91.8

TABLE 5

Dehydrogenation of Isopropyl Alcohol

Alcohol feed of 1.05 ml in 5 minutes; theoretical amount of H_2 from 1.05 ml of alcohol = 308 ml

Experiment	Temperature (°C)	Amount of H_2 from 1.05 ml of alcohol (ml at STP)	Degree of dehydrogenation from amount of H_2 (%)	Analysis of gas (% by volume)		
				CO_2	Unsaturated hydrocarbons	H_2
40	271	26	8.4	Not analyzed		
7	283	62	20.2	0.0	0.2	99.8
12	285	64	20.8	0.0	0.2	99.8
38	292	76	24.7	0.2	0.2	99.6
39	293	76	24.7	0.2	0.2	99.6
6	296	90	29.2	0.2	0.2	99.6
2	296	90	29.2	0.2	0.4	99.4
3	298	91	29.5	0.0	0.2	99.7
13	305	94	30.5	0.2	0.4	99.4
37	312	107	34.7	0.2	0.2	99.6
41	312	107	34.7	0.2	0.4	99.2
4	317	118	38.4	0.2	0.6	99.2
14	324	122	39.6	0.4	0.4	99.2
5	329	141	45.8	0.2	0.8	99.0
15	337	166	54.0	0.2	0.4	99.4
22	336	164	53.4	0.8	1.4	97.8

Experiments with Ethyl Alcohol. Experiments were carried out at 345–405° with rates of passage of alcohol (v) of 0.5, 0.8, and 1.0 ml in five minutes. The conversion of alcohol into aldehyde was 10–47% (Table 3, Fig. 1). For $v = 1.0$ ml in 5 minutes and a low conversion, the hydrogen content of the gas attained 98.4% and the content of unsaturated hydrocarbons did not exceed 0.4–0.6%. With rise in temperature to 405° and also reduction in v to 0.5 ml in 5 minutes, the content of unsaturated hydrocarbons in the gas increased and the hydrogen concentration fell to 92%.

TABLE 6

Dehydrogenation of Allyl Alcohol

Experiment	Temperature (°C)	Amount of H ₂ from 1 ml of alcohol (ml at STP)	Degree of dehydrogenation from amount of H ₂ (%)	Analysis of gas (%) by volume)		
				CO ₂	Unsaturated hydrocarbons	H ₂
Alcohol feed of 1 ml in 5 minutes; theoretical amount of H ₂ from 1 ml of alcohol = 329,6 ml						
35	332	15	4.5	0.6	0.0	99.4
36	352	23,6	7.1	1.4	0.0	98.6
37	378	41,3	12.5	2.6	0.0	97.4
38	400	64,5	19.5	4.4	0.4	95.2
39	420	94,0	28.5	6.0	1.6	92.4
Alcohol feed of 1.2 ml in 5 minutes; theoretical amount of H ₂ from 1.2 ml of alcohol = 405 ml						
41	380	45.9	11.3	2.0	0.0	98.0
46	400	69.4	17.1	3.4	0.2	96.4
43	422	108.5	26.8	5.2	2.0	92.8

For the determination of relative absorption coefficients of acetaldehyde, the rates of dehydrogenation of alcohol-acetaldehyde mixtures containing 75 and 50% of alcohol were investigated. The experiments were carried out at 345°, 366°, and 387° with $v = 1.0$ ml in 5 minutes. With rise in temperature the relative adsorption coefficient of acetaldehyde diminished, the change being from 2.3 at 345° to 0.73 at 387° (Table 7, Fig. 2).

Experiments with Propyl Alcohol. The measurements were carried out over the temperature range 293–425° and at $v = 1.05$ ml in 5 minutes. The conversion of alcohol into aldehyde was 8.3–92.4% (Table 4). The degree of conversion increased with rise in temperature and at 422–425° it attained 88.2–92.4%. The amount of unsaturated hydrocarbons in the gas did not exceed 0.2–0.4%. The relative absorption coefficient of propionaldehyde z_2 was temperature-dependent, as in the case of acetaldehyde; with rise in temperature it diminished from 3.56 at 342° to 1.71 at 391° (Table 7, Fig. 2).

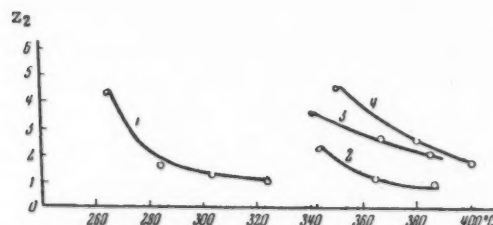


Fig. 2. Dependence of z_2 on temperature: 1) isopropyl alcohol; 2) ethyl alcohol; 3) propyl alcohol; 4) allyl alcohol.

conditions the conversion of the alcohol was 8.4–54% (Table 5). The hydrogen concentration in the gas varied in the range 99–99.8%. The content of unsaturated hydrocarbons in the gas did not exceed 0.2%. The relative adsorption coefficient of acetone – determined from the changes in rate of dehydrogenation of alcohol-acetone mixture in the range 265–325° – varied with rise in temperature from 4.34 at 265° to 0.95 at 325° (Table 7, Fig. 2). At 368° and $v = 0.5$ ml in 5 minutes, the conversion of isopropyl alcohol attained 95.7% with the same content of hydrogen in the gas.

Experiments with Allyl Alcohol. Experiments with allyl alcohol were carried out over the temperature range 332–422° and at $v = 1.0$ and 1.2 ml in 5 minutes. The conversion of alcohol into aldehyde was 4.5–28.5% (Table 6). The concentration of hydrogen in the gas was 96.2–99.4%, and that of unsaturated hydrocarbons was 0.4%. Experiments with alcohol-aldehyde mixtures were carried out at 352°, 381°, and 402° and at $v = 1.0$ and 1.12 ml in 5 minutes. The relative adsorption coefficient of acrolein over the stated temperature range varied from 4.54 at 352° to 1.65 at 402° (Table 7, Fig. 2).

Experiments with Isopropyl Alcohol. The measurements were carried out in the temperature range 271–336° and at $v = 1.05$ ml in 5 minutes. Under these

TABLE 7

Adsorption Coefficients and Thermodynamic Functions Calculated from Them

Substance	Temperature (°C)	Alcohol content of mixture (%)		z_2 , mean	ΔF (cal)	ΔH (kcal)	ΔS (cal./mole degree)
1	2	3	4	5	6	7	8
Acetaldehyde	345	2.25	2.45	2.3	-1022		-33.9
	366	1.1	0.9	1.0	-292	-22.0	-34.0
	387	0.6	0.87	0.73	+ 102.9		-34.0
Propionaldehyde	342	3.42	3.7	3.56	-1550		-15.7
	368	2.9	2.1	2.5	-1166	-11.2	-15.6
	386	1.9	1.98	1.94	-866.8		-15.6
	391	1.7	1.72	1.71	-		-
Acrolein	352	4.54	-	4.54	-1872		-23.2
	381	2.43	-	2.43	-1152	-16.4	-23.3
	402	1.65	-	1.65	-671		-23.3
Acetone	265	4.63	4.06	4.34	-		-
	285	1.33	1.83	1.60	-520.4		-18.2
	305	1.23	-	1.23	-237.5	-11.0	-18.2
	325	0.8	1.1	0.95	+ 60.9		-18.3

Using the relative adsorption coefficients found for aldehydes and acetone on catalytically active centers (Table 7) and applying the following equation [9] to these data —

$$\Delta F(A_2, A_1) = -RT \log z_2, \quad (2)$$

we can find the free energy ΔF for the displacement of alcohol by aldehyde or ketone from the active surface. In Column 6 of Table 7 we give the values of ΔF found. The results show that aldehyde (or ketone) vapor should retard the dehydrogenation of an alcohol into the aldehyde owing to adsorptional displacement, and the experimental results confirm this.

Figure 3 shows the relation between $\log z_2$ and the reciprocal of temperature; it will be seen that the points fit closely to straight lines. Values of ΔH were calculated from the slopes of the lines by use of the equation

$$\Delta H = 4.57 \frac{T_2 T_1}{T_2 - T_1} \log \frac{(z_2) T_2}{(z_2) T_1}. \quad (3)$$

The resulting values of ΔH are given in Column 7 of Table 7.

From the values obtained for ΔH and ΔF , ΔS was calculated (Column 8 of Table 7), the formula used being

$$\Delta S = \frac{\Delta H - \Delta F}{T}. \quad (4)$$

Hence, experiments with alcohols with a given number of carbon atoms in the molecule showed that the activity and selectivity of the catalyst depend on the structure of the alcohol — on the position of the hydroxy group in the molecule and the presence or absence of an ethylenic bond. The presence of an ethylenic bond in the alcohol molecule has the greatest effect on the rate of the dehydrogenation reaction. The rate of dehydrogenation of allyl alcohol is much lower than that of propyl alcohol. The secondary alcohol was dehydrogenated more readily than the primary alcohols. Calculations of the rate constants of the reaction on the basis of the results obtained here will be made in the following communication.

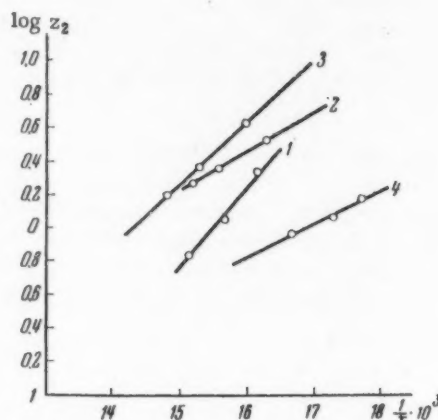


Fig. 3. Dependence of $\log z_2$ on the reciprocal of temperature: 1) ethyl alcohol; 2) propyl alcohol; 3) allyl alcohol; 4) isopropyl alcohol.

SUMMARY

1. Data were obtained on the kinetics of dehydrogenation of ethyl, propyl, allyl, and isopropyl alcohols over an oxide catalyst.
2. It was found that the catalyst acted selectively and brought about dehydrogenation of the alcohols to aldehydes (ketones). The dehydration reaction was almost absent.
3. It was shown that, in the temperature range investigated, the relative adsorption coefficients of aldehydes (and acetone) are temperature-dependent — diminishing with rise of temperature. The adsorption coefficient of hydrogen is substantially zero.
4. The changes of free energy, enthalpy, and entropy were determined for adsorptional displacement from the catalytically active surface.

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EFFECT OF THE MOLECULAR STRUCTURE OF AN ALCOHOL ON THE KINETICS OF ITS DEHYDROGENATION

COMMUNICATION 2. C₄-C₈ ALCOHOLS

O. K. Bogdanova, A. A. Balandin, and A. P. Shcheglova

In the previous communication [1] we gave some data on the kinetics of the dehydrogenation of ethyl, propyl, allyl, and isopropyl alcohols over an oxide catalyst. We now describe the kinetics of the dehydrogenation of butyl, isopentyl, and phenethyl alcohols, and we also discuss the results of the first series of experiments with C₂ and C₃ alcohols.

EXPERIMENTAL

In our study of the kinetics of the dehydrogenation of C₄-C₈ alcohols we used the same procedure as in the previous work. The same oxide catalyst was used. The rate of reaction was determined from the volume of hydrogen liberated. The catalyzate was analyzed for aldehyde content. Close correlation was observed between the amounts of hydrogen liberated and of aldehyde formed. The aldehydes required in experiments on the relative adsorption coefficients of reaction products were isolated as before from the catalyzates by distillation, dried with sodium sulfate, and distilled. Table 1 gives the constants of the alcohols and corresponding aldehydes together with data from the literature.

TABLE 1

Substance	Experimental values			Data from literature [2,3]		
	B.p. (°C)	d_4^{20}	n_D^{20}	B.p. (°C)	d_4^{20}	n_D^{20}
Butyl alcohol	117—117.5	0.8098	1.3992	117.5	0.810	1.3992
Isopentyl alcohol	129—129.5	0.8126	1.4082	128.5—9.5	0.816	1.4087 (25°)
Phenethyl alcohol	110.2 (16 mm)	1.02225	1.5330	104—105 (14 mm)	1.023 (15°)	1.52673
Butyraldehyde	74.7	0.8168	1.3844	74—75	0.817	1.38433
Isovaleraldehyde	91—93	0.8057	—	90—92	0.8068 (20°)	—
Phenylacetaldehyde	92—93 (22 mm)	—	1.5320	85—86 (10 mm)	1.0252	1.53191

Experiments with Butyl Alcohol. The experiments were carried out at temperatures ranging from 320° to 386° with rates of passage of butyl alcohol (v) of 1.05 and 0.8 ml in 5 minutes. The conversion of alcohol into aldehyde was 13.6—51.7% (Table 2). The hydrogen content of the gas collected attained 99%, and the

concentration of unsaturated hydrocarbons did not exceed 0.2-0.4%.

For the determination of the relative adsorption coefficients of butyraldehyde we investigated the rates of dehydrogenation of binary mixtures of butyl alcohol and butyraldehyde containing 75% and 50% of alcohol. The experiments were carried out at 322°, 344°, and 366° and $v = 1.05$ ml in 5 minutes. As in the case of the C_2 and C_3 alcohols, the relative adsorption coefficient of butyraldehyde fell (5.7 at 322° and 2.7 at 366°, see Table 5 and Fig. 1).

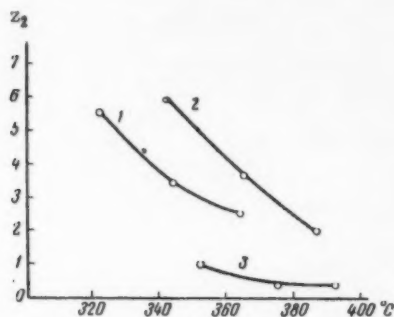


Fig. 1. Dependence of relative adsorption coefficients (z_2) on temperature: 1) butyraldehyde; 2) isovaleraldehyde; 3) phenylacetaldehyde.

Experiments with Isopentyl Alcohol. The experiments were carried out at temperatures ranging from 324° to 410° with $v = 1.05$ ml in 5 minutes. Over this temperature range the degree of dehydrogenation of isopentyl alcohol into the aldehyde was 16-73%. The gas contained 99-99.2% of hydrogen and 0.2-0.4% of unsaturated hydrocarbons. At 410° the concentration of unsaturated hydrocarbons in the gas rose to 0.8% (Table 3). Measurements of dehydrogenation rates for binary alcohol-aldehyde mixtures (75% and 50% of the alcohol) were carried out at 342°, 365°, and 387° with $v = 1.05$ ml in 5 minutes. It was found that the relative adsorption coefficient of the aldehyde was temperature-dependent and fell from 6.06 at 342° to 2.12 at 387° (Table 5, Fig. 1).

TABLE 2

Dehydrogenation of Butyl Alcohol

Experiment	Temperature °C	H ₂ (ml at STP)	Degree of dehydrogenation from amount of H ₂ (%)	Analysis of gas (% by volume)		
				CO ₂	Unsaturated hydrocarbons	H ₂
v = 1.05 ml in 5 minutes; theoretical amount of H ₂ from 1.05 ml of alcohol = 257 ml						
12	320	35	13.6	0.8	0.2	99.0
11	341	52	20.2	0.8	0.2	99.0
10	363	83	32.3	1.0	0.4	98.6
9	386	133	51.7	0.8	0.2	99.0
v = 0.8 ml in 5 min; theoretical amount of H ₂ from 0.8 ml of alcohol = 196 ml.						
4	322	32	16.3	0.6	0.2	99.2
2	366	78	39.8	1.0	0.3	98.7

Experiments with Phenethyl Alcohol. Measurements were carried out at 349-392° and $v = 1.4$ and 1.17 ml in 5 minutes. Under these conditions the conversion of phenethyl alcohol was 17.2-43.3% (Table 4). Unsaturated hydrocarbons were absent from the gas, and the hydrogen content was 97.2-95%, at 392° the amount of hydrogen was reduced to 93.2%.

The relative adsorption coefficient of phenylacetaldehyde, determined from the rate of dehydrogenation of mixtures of phenethyl alcohol and the aldehyde varied from 1.06 at 352° to 0.5 at 374° (Table 5, Fig. 1).

By substituting the values found for the relative adsorption coefficients of the aldehydes at the catalytically active centers in the same equations as in the preceding paper [1], we found free energies of displacement of alcohol by aldehyde from the active surface and calculated the enthalpy and entropy changes. The values obtained are given in Columns 6-8 of Table 5. Figure 2 shows the relation between $\log z_2$ and the reciprocal of temperature. The points fit well to straight lines.

TABLE 3

Dehydrogenation of Isopentyl Alcohol

(v = 1.05 ml in 5 minutes; theoretical amount of H₂ from 1.05 ml of alcohol = 218 ml)

Experiment	Temperature (°C)	H ₂ (ml at STP)	Degree of dehydrogenation from amount of H ₂ (%)	Analysis of gas (% by volume)		
				CO ₂	Unsaturated hydrocarbons	H ₂
2	324	35	16.0	0.6	0.2	99.2
1	342	54	24.8	0.6	0.4	99.0
3	365	78	35.8	0.4	0.4	99.2
4	387	112	51.4	0.4	0.4	99.2
5	410	161	73.8	0.4	0.4	99.2

TABLE 4

Dehydrogenation of Phenethyl Alcohol

Experiment	Temperature (°C)	H ₂ (ml at STP)	Degree of dehydrogenation from amount of H ₂ (%)	Analysis of gas (% by volume)		
				CO ₂	Unsaturated hydrocarbons	H ₂
v = 1.4 ml in 5 minutes; theoretical amount of H ₂ from 1.4 ml of alcohol = 263.7 ml						
14	349	45.5	17.2	2.8	0.0	97.2
17	366	68.0	25.8	4.2	0.0	95.8
18	372	76.2	28.8	4.4	0.0	95.6
15	374	79.8	30.8	5.0	0.0	95.0
16	392	114.4	43.3	6.8	0.0	93.2
v = 1.17 ml in 5 minutes; theoretical amount of H ₂ from 1.17 ml of alcohol = 220 ml						
20	360	46.0	23.6	3.8	0.0	96.2
4	395	96.6	43.5	7.8	0.0	92.2
21	395	98.1	43.9	8.0	0.0	92.0

TABLE 5

Thermodynamic Functions for the Process of Displacement of Alcohol by Aldehyde

Aldehyde	Temperature (°C)	Amount of alcohol (%)		z ₂ , mean	ΔF (cal/ /mole)	ΔH (kcal)	ΔS (cal /mole degree)
		75	50				
		z ₁					
t	2	3	4	5	6	7	8
Butyraldehyde	322	5.48	5.70	5.6	—2030	—11.3	—15.6
	344	3.0	4.0	3.5	—1530		—15.8
	366	2.68	2.7	2.7	—1200		—15.7
Isovaleraldehyde	342	6.06	—	6.06	—2195	—17.5	—24.8
	365	3.5	4.0	3.75	—1660		—24.8
	387	2.12	—	2.12	— 984, 2		—25.0
Phenylacetalde- hyde	352	0.9	1.22	1.06	— 224, 0	—27.5	—43.8
	366	0.65	—	0.65	+ 545, 4		—43.9
	374	0.5	0.5	0.5	+ 842		—43.9

For the calculation of rate constants for the dehydrogenation of alcohols we used the general kinetic equation for unimolecular catalytic reactions in a flow system derived by one of the authors [4] on the basis of the equation:

$$\frac{dx}{dt} = k \frac{[A_1]}{[A_1] + z_2 [A_2] + z_3 [A_3]} \quad (1)$$

For the case of the dehydrogenation of alcohols, for which the relative adsorption coefficient of hydrogen $z_3 = 0$ [1], the equation assumes the form:

$$2.303A_1 z_2 \log \frac{A_1}{A_1 - m(z_2 - 1)} - m(z_2 - 1) = k. \quad (2)$$

The rate constants for the dehydrogenation of alcohols from ethyl to phenethyl, inclusive, calculated from the experimental data with the aid of Equation 2 are given in Table 6. It is very significant that the rate constants found from Equation 2 for different space velocities were found to be very close in value. This provides confirmation of the correctness of Equation 2.

The true activation energies, as found from the rate constants for the alcohols, are given in Table 6. Attention should be turned on the fact that the apparent (i.e. found from the reaction rates at low percent conversion) and true (i.e. found from the rate constants) activation energies differ only a little for all the alcohols investigated, the true value being always somewhat higher than the apparent value. In Figure 3, which was constructed on the basis of the data in Table 6, logarithms of the dehydrogenation rate constants of the seven alcohols are plotted as ordinates and reciprocals of the absolute temperature as abscissae. It will be seen that the alcohols fall in a definite order; the points fall satisfactorily on straight lines so that the Arrhenius equation is fulfilled. The rate constants for the dehydrogenation of the alcohols rise from allyl (lowest rate of dehydrogenation) to isopentyl alcohol. Under given dehydrogenation conditions, the rate of reaction of isopropyl alcohol is considerably higher than that of the other alcohols examined. For comparison purposes, experimental and interpolated data for the rates of dehydrogenation of the alcohols investigated are given for the same temperature (345°) in Table 7.

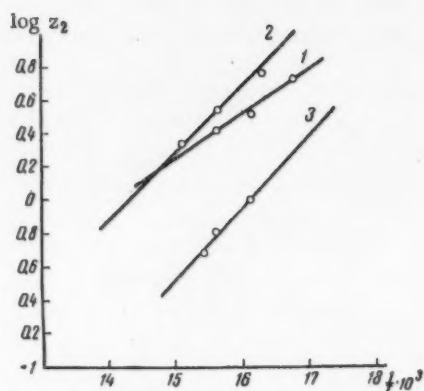


Fig. 2. Dependence of $\log z_2$ on the reciprocal of temperature: 1) butyl alcohol; 2) isopentyl alcohol; 3) phenethyl alcohol.

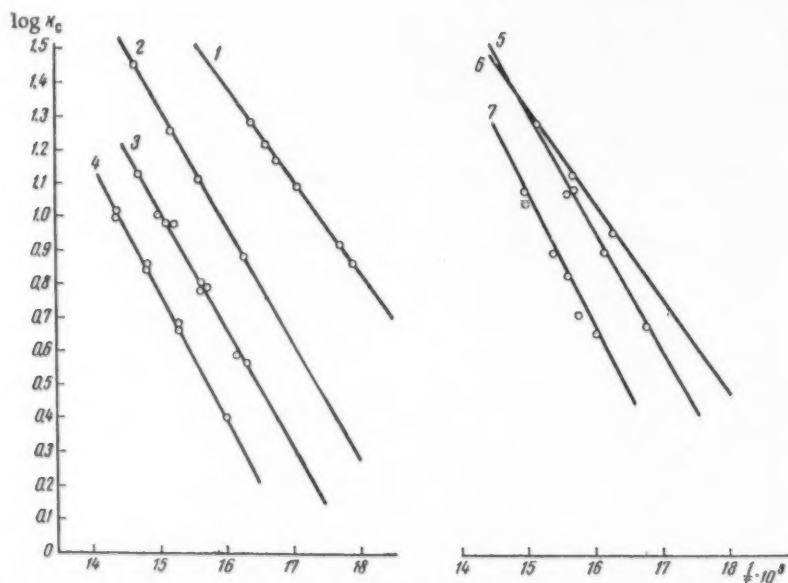


Fig. 3. Dependence of $\log k_c$ on the reciprocal of temperature: 1) isopropyl alcohol; 2) propyl alcohol; 3) ethyl alcohol; 4) allyl alcohol; 5) butyl alcohol; 6) isopentyl alcohol; 7) phenethyl alcohol.

TABLE 6

Rate Constants and Activation Energies for the Dehydrogenation of Alcohols

Alcohol	Temperature (°C)	k_c (per ml of catalyst)	ϵ (cal/mole)	log k_0
Ethyl	345	3.83	17 700	6.85
	366	6.07		
	387	9.6		
Propyl	342	7.56	15 600	6.43
	368	12.9		
	386	18.1		
Allyl	352	2.5	17 500	6.53
	378	4.56		
	400	6.87		
Isopropyl	285	7.21	12 800	5.87
	312	12.3		
	329	16.6		
Butyl	322	4.82	16 300	6.68
	344	8.02		
	364	11.9		
Isopentyl	342	9.65	12 900	5.57
	365	13.55		
	387	18.9		
Phenethyl	349	4.6	18 000	6.99
	366	6.84		
	374	7.9		

TABLE 7

Values of k_c and ΔF for Various Alcohols at 345°

Alcohol	Temperature 345°			
	z_s	k_c (per ml of catalyst)	ΔF (cal/mole)	ΔS (cal/mole, degree)
Phenethyl	1.2	4.27	-223.6	-43.9
Ethyl	2.3	3.83	-1020	-33.7
Allyl	5.1	2.09	-1899	-23.8
Propyl	3.4	8.8	-1501	-15.7
Butyl	3.5	6.07	-1530	-15.8
Isopentyl	5.75	10.0	-2148	-24.8
Isopropyl	0.8	21.9	+273.7	-18.8

The relation between degree of dehydrogenation and temperature is shown in Figure 4 (ordinates - degree of dehydrogenation; abscissae - temperature). Calculation of the logarithm of the pre-exponential factor of the Arrhenius equation (k_0) for all the alcohols gave the results shown in Table 6.

A more detailed examination of the kinetic characteristics found will be given elsewhere.

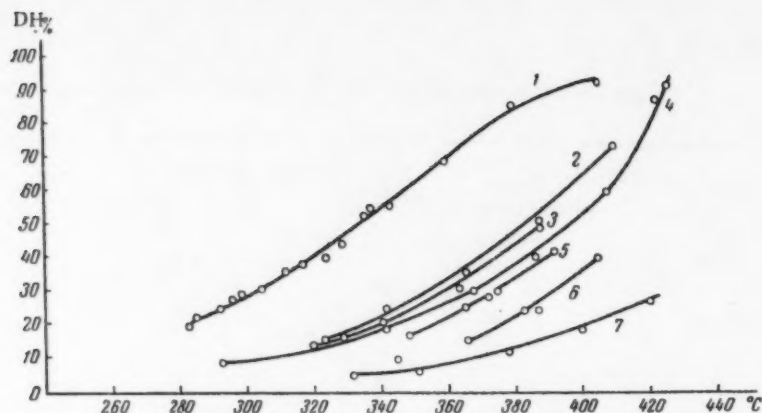


Fig. 4. Effect of temperature on degree of dehydrogenation (DH): 1) isopropyl alcohol; 2) isopentyl alcohol; 3) butyl alcohol; 4) propyl alcohol; 5) phenethyl alcohol; 6) ethyl alcohol; 7) allyl alcohol.

SUMMARY

1. The kinetics of the dehydrogenation of butyl, isopentyl, and phenethyl alcohols over an oxide catalyst were investigated.
2. It was shown that the catalyst acts selectively and promotes the dehydrogenation of the alcohols: dehydration is almost absent, this being shown by the low content (0.2–0.4%) of unsaturated hydrocarbons in the gas formed.
3. It was found that the relative adsorption coefficients of the aldehyde products are temperature-dependent, diminishing with rise in temperature.
4. Free energy, enthalpy, and entropy changes were determined for adsorptional displacement from the catalytic surface.
5. Rate constants were determined for the dehydrogenation of the following seven alcohols: allyl, ethyl, propyl, butyl, isopentyl, isopropyl, and phenethyl. The true activation energies were determined.

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INVESTIGATION OF THE OXIDATION OF METHANE WITH THE AID OF LABELED ATOMS

COMMUNICATION 2. MECHANISM OF THE FORMATION OF CARBON DIOXIDE

R. I. Moshkina, A. B. Nalbandyan, M. B. Neiman, and G. I. Feklisov

In a previous paper [1] we have shown that, in the thermal oxidation of methane catalyzed by oxides of nitrogen, carbon monoxide — the main carbon-containing reaction product — is formed mainly from formaldehyde by oxidation or decomposition. The present paper describes an investigation of the ways in which carbon dioxide may be formed. The question of whether the dioxide is formed from the monoxide by its further oxidation or directly from other intermediate products of the oxidation of methane is of fundamental importance in the development of a scheme for the oxidation of methane at high temperatures. This problem was solved by the kinetic tracer method [2].

EXPERIMENTAL

The work was carried out in the flow apparatus shown diagrammatically in Fig. 1. In order to initiate reaction and obtain appreciable amounts of carbon dioxide, 0.7% of nitric oxide was added to the reaction mixture, which contained 80% of methane and 20% of oxygen. It should be noted that for periods of contact of about 7 seconds the uncatalyzed reaction (oxides of nitrogen absent) does not go at all below 650°.

The methane was obtained from a cylinder and was carefully purified from traces of carbon dioxide. Carbon monoxide labeled with radioactive carbon and the oxides of nitrogen were carefully freed from traces of carbon dioxide and were preserved in gas holders over saturated brine. The amounts of gas passed to the reactor were measured with flowmeters. The gases leaving the reactor were scrubbed with saturated brine in a scrubber having a glass filling, in order to remove formaldehyde and methanol, and were then passed to gas holders and analyzed for their contents of carbon monoxide and dioxide.

The CO labelled with radioactive carbon which was required for this work was obtained in a special circulation apparatus by the reaction:



The zinc was in the form of dust, supported on asbestos, and the reaction was carried out at about 400° [3]. Circulation of the gas made it possible to increase the yield of labeled carbon monoxide to 98% on the original C^{14}O_2 . Purification of the C^{14}O from residual C^{14}O_2 was effected by "isotopic dilution" with carbon dioxide followed by freezing out the whole of the carbon dioxide with liquid nitrogen.

The amount of carbon monoxide and dioxide in the oxidation products from methane was determined in an Orsat apparatus and also gravimetrically by converting these gases into barium carbonate. From the precipitates so obtained samples were prepared for the determination of the specific activities α_{CO} and α_{CO_2} . Activities were measured with an end-window counter.

We carried out special experiments in order to determine whether exchange could occur between carbon monoxide and dioxide under the conditions of the main experiments. These experiments differed from the kinetic experiments in that oxygen was replaced by an equal amount of methane and the higher temperature

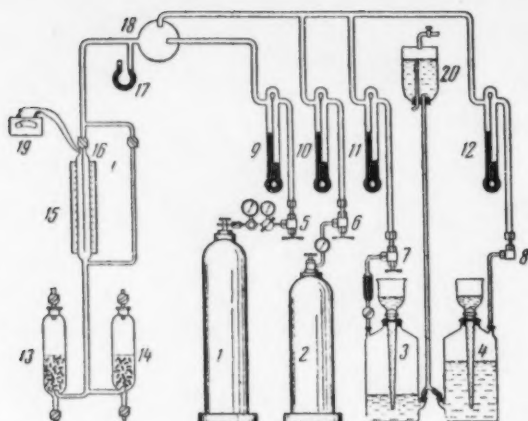


Fig. 1. Diagram of experimental arrangement: 1, 2) cylinders of oxygen and methane; 3) gas holder containing oxides of nitrogen; 4) gas holder containing labeled carbon monoxide; 5-8) valves; 9-12) flowmeters

of 645° was used; the time of contact was 4 seconds. The $C^{14}O_2$ and CO_2 contents of the mixture were 0.3 and 0.8% respectively. In these experiments the specific activity of the original carbon monoxide was 1.6 μ curie/mole. Determination of the specific activities of the gases leaving the reactor showed that under these conditions no exchange occurred between the labeled carbon monoxide and carbon dioxide. The specific activity of the carbon dioxide leaving the reactor was zero, but that of the carbon monoxide was 1.14 μ curie/mole.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Introduction of labeled carbon monoxide into the oxidation reaction of methane, the final products of which are CO , CO_2 , and H_2O , would be expected to lead a variation with time of the specific activities α_{CO} and α_{CO_2} in accordance with the laws:

$$\frac{d\alpha_{CO}}{dt} = - \frac{\alpha_{CO} \cdot w}{[CO]} \quad (1)$$

$$\frac{d\alpha_{CO_2}}{dt} = \frac{\left(\alpha_{CO} - \alpha_{CO_2} \cdot \frac{w_1 + w_2}{w_1} \right) \cdot w_1}{[CO_2]} \quad (2)$$

in which w_1 is the rate at which carbon dioxide is formed directly from carbon monoxide and w_2 is the rate at which it is formed from other substances.

Let us examine Equation 2 in detail. In order to obtain a qualitative picture of the change in the activity of carbon dioxide, let us consider the following extreme cases:

a) Let carbon dioxide be formed preferentially from carbon monoxide, i.e., $w_1 > w_2$. In this case for the rate of change of α_{CO_2} we have:

$$\frac{d\alpha_{CO_2}}{dt} = \frac{(\alpha_{CO} - \alpha_{CO_2}) w_1}{[CO_2]} \quad (3)$$

and since

$$\frac{d\alpha_{CO_2}}{dt} < 0 \text{ hence, } \alpha_{CO_2} > \alpha_{CO}$$

This means that, in the case of the sequence of reactions $\text{HCHO} \rightarrow \text{CO} \rightarrow \text{CO}_2$, at each point of time (except $t = 0$) the specific activity of carbon dioxide must be higher than that of carbon monoxide — which is quite understandable and natural. In fact, at each point of time the specific activity of carbon dioxide is the averaged sum of the activities of carbon monoxide in the period preceding the given point of time.

b) If carbon dioxide is formed preferentially not from carbon monoxide but from other substances, then $w_2 \gg w_1$. In the limiting case, when $w_1 = 0$, the specific activity $\alpha_{\text{CO}_2} = 0$. When w_1 is small in comparison with w_2 , $\alpha_{\text{CO}_2} < \alpha_{\text{CO}}$.

Experimental kinetic curves for the accumulation of carbon monoxide and dioxide in the oxidation of methane in presence of 0.9% of labeled carbon monoxide at 575° are shown in Figure 2. It will be seen that, for the times of contact investigated (1–7 seconds), the yields of these products increase. Curves for the changes in the specific activities of carbon monoxide (1) and carbon dioxide (2) as functions of time of contact are shown in Figure 3. As would be expected, the specific activities of these substances fall rapidly with time. The curve for the variation in the specific activity of carbon monoxide α_{CO} is always considerably higher than that for carbon dioxide (α_{CO_2}). In accordance with the case (b) considered above, such a disposition of the specific activity curves indicates that much of the carbon dioxide is formed from substances other than carbon monoxide. For the determination of the proportion of the CO_2 that is formed from CO , experiments may be carried out with mixtures containing a known amount of carbon dioxide. As shown in the previous investigation, by this method, from the intersection of the maximum of the α_{CO_2} curve with the α_{CO} curve, it is possible to resolve the question of the mechanism of the formation of carbon monoxide. However, as is not difficult to see, the curve for the variation of α_{CO_2} can be obtained by recalculation of the data on the variation of α_{CO_2} with time, without carrying out experiments with addition of CO_2 to the original mixture.

For this purpose it is sufficient to assume that the original mixture contains some particular amount of carbon dioxide and calculate new spe-

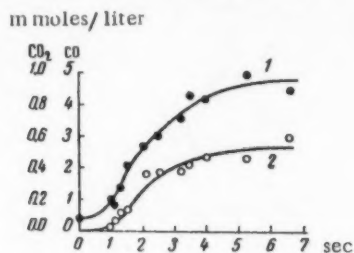


Fig. 2. Kinetics of the accumulation of 1) carbon monoxide, 2) carbon dioxide.

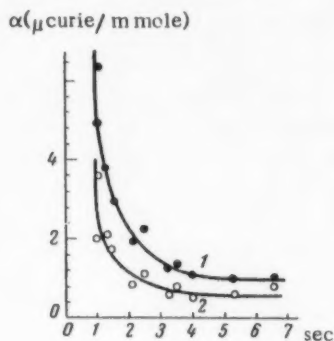


Fig. 3. Variation in specific activity: 1) carbon monoxide; 2) carbon dioxide.

cific activities α_{CO_2} as a function of time from the existing experimental data on α_{CO_2} . Figure 4 gives curves for the variation of specific activity of carbon dioxide (1, 2, and 3) recalculated from the α_{CO_2} curve on the assumption that the original mixture contains 0.1, 0.15, and 0.2 mmole/liter of CO_2 . The curves have characteristic maxima, but at these maxima the specific activity of carbon monoxide (Curve 4) is about four times as great as α_{CO_2} . This indicates that in times of contact of 1.25–1.6 seconds about 75% of the carbon dioxide is formed without passing through the stage of carbon monoxide. The fact that only an insignificant proportion of the carbon monoxide is oxidized to CO_2 can be seen also from the activity balance. Figure 5 gives curves for the variations of the total activities of CO (Curve 1) and CO_2 (Curve 2) with time. Within the limits of the experimental error, which is associated mainly with the feed of C^{14}O to the reacting mixture, the total activity of carbon monoxide $I_{\text{CO}} = \alpha_{\text{CO}}[\text{CO}]$ remains almost constant at 5.2 μcuries . The total activity of carbon dioxide, $I_{\text{CO}_2} = \alpha_{\text{CO}_2}[\text{CO}_2]$, at first rises with time and then remains constant; it attains 0.26 μcurie , i.e., much less than I_{CO} . We come to the same result when we compare the rates of formation of CO and CO_2 . The rate of formation of CO_2 from CO may be calculated from the formula:

$$w_1 = \frac{1}{\alpha_{\text{CO}}} \cdot \frac{dI_{\text{CO}_2}}{dt} \quad (4)$$

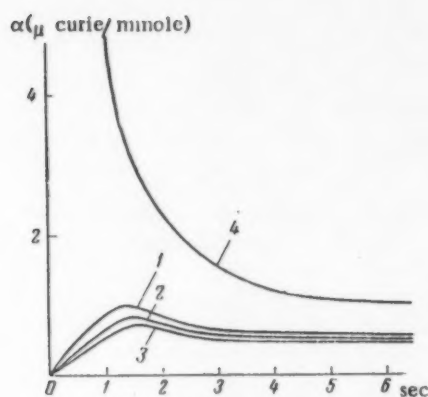


Fig. 4. Calculated curves for the specific activity of carbon dioxide in the oxidation reaction of methane with addition of CO_2 of 1) 0.1 mmole/liter, 2) 0.15 mmole/liter, and 3) 0.2 mmole/liter; Curve 4 represents the specific activity of C^{14}O .

CO is consumed slowly and that the bulk of the carbon dioxide is therefore formed from other intermediate products.

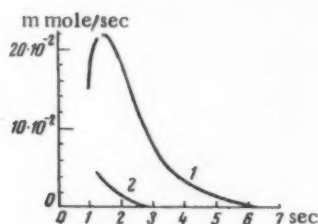
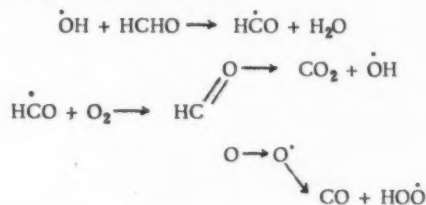


Fig. 6. Rate of formation of carbon dioxide from carbon monoxide (Curve 2) and rate of accumulation of carbon dioxide (Curve 1).

The question of the precursors of CO_2 remains open for the present. It is not yet clear whether carbon dioxide is formed directly from formaldehyde by the scheme



or is formed from formic acid by its oxidation or decomposition. This question will form the subject of further investigations.

SUMMARY

1. It was shown by a kinetic method that carbon monoxide is not the sole precursor of carbon dioxide

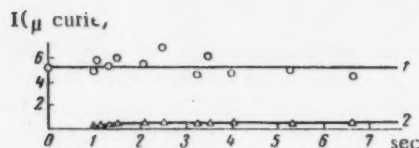


Fig. 5. Total activity: 1) carbon monoxide; 2) carbon dioxide.

The total rate of formation of carbon dioxide $w = w_1 + w_2$ was found by graphical differentiation of the kinetic curve for the accumulation of CO_2 (see Figure 2). The results of the calculation are given in Figure 6. Curve 2 of this figure represents the rate of formation of CO_2 from CO , and Curve 1 represents the total rate of formation of CO_2 . It will be seen from Figure 6 that the rate of formation of CO_2 from CO is relatively low. Let us examine, finally, the rates of formation and accumulation of carbon monoxide. The rate of formation of CO can be calculated from Equation 1, and the rate of its accumulation from the kinetic Curve 1 of Figure 2. The results of the calculations are shown in Figure 7 (o - rates of formation of CO ; x - rate of its accumulation). The points are disposed around an average curve. This indicates that

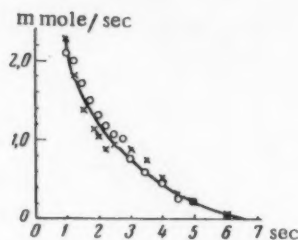


Fig. 7. Rate of accumulation of carbon monoxide (x) and rate of its formation (o).

in the oxidation of methane.

2. Comparison of rates of accumulation of CO_2 with the rate of its formation from CO shows that only about 25% of the CO_2 is formed by the oxidation of CO.

3. By the reduction of C^{14}O_2 with zinc, C^{14}O of high activity was obtained in 98% yield.

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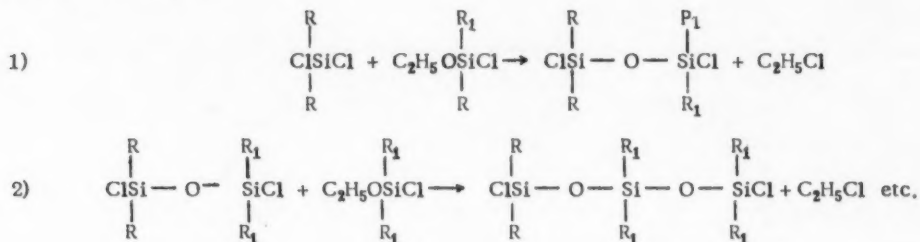
ORGANIC AND BIOLOGICAL CHEMISTRY

SYNTHESIS OF ALKYLCHLOROSILOXANES BY HETEROFUNCTIONAL CONDENSATION

N. N. Sokolov and K. A. Andrianov

In previous papers we have described new reactions for the formation of polyorganosiloxanes based on interaction between the functional groups of organosilicon monomers [1, 2]. It was found that, in presence of catalysts, acetoxy-, chloro-, and alkoxy-alkyl (or aryl) silanes react with one another with formation of polyorganosiloxanes. It is of interest to make use of these reactions for the synthesis of organosilicon compounds of low molecular weight, particularly those which are difficult to prepare by other methods.

In this investigation we have studied the condensations of dichlorodimethylsilane, dichloromethylsilane, dichlorodiethylsilane, and dichloroethylsilane with chloroethoxydimethylsilane. Anhydrous ferric chloride (0.5% on the reaction mixture) was used as catalyst. The experiments showed that in the condensation of dichlorodiethylsilane and of dichlorodimethylsilane with chloroethoxydimethylsilane reaction proceeds by stepwise condensation:



In the condensation of dichloromethylsilane and of dichloroethylsilane with chloroethoxydimethylsilane, apart from this main reaction there occur also complicating disproportionation reactions. In the condensation of one mole of dichlorodimethylsilane with one mole of chloroethoxydimethylsilane, three linear chloromethylsiloxanes were isolated (Table 1; the yields are based on the total amount of chlorosilanes taken) and 22% of the dichlorodimethylsilane taken for reaction was recovered unchanged.

No unchanged chloroethoxydimethylsilane and no cyclic compounds were detected among the condensation products. Analysis indicated that the residue in the still contained a mixture of penta- and hexa-siloxanes of this series.

The same compounds in approximately the same proportions were isolated [3] as a result of the hydrolysis of dichlorodimethylsilane with insufficient water in a diethyl ether medium. This shows that the condensation of dichlorodimethylsilane with chloroethoxydimethylsilane results in the formation of chlorodimethylsiloxanes having mainly 2-4 silicon atoms in the molecule, the process proceeding according to the above-indicated scheme of stagewise reaction.

In the condensation of dichlorodiethylsilane and chloroethoxydimethylsilane taken in equimolecular proportions it was found that only one-third of the former reacted, whereas the latter reacted completely. The chloroalkylsiloxanes then formed contained mainly 4-5 silicon atoms per molecule. Hence, in order to isolate the initial condensation products the amount of dichlorodiethylsilane was raised to two molecular proportions. In this way some new compounds were obtained (Table 2) and it was shown that, as in the previous case,

TABLE 1

Substance	Formula	B.p. (°C at 738 mm)	Yield (%)	Data in literature [3]	
				B.p. (°C at 760 mm)	Yield (%)
1,3-Dichloro-1,1,3,3-tetramethyldisiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{ClSi} - \text{O} - \text{SiCl} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	135.5	27.5	138	28
1,5-Dichloro-1,1,3,3,5,5-hexamethyltrisiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{ClSi} - \left[\text{O} - \text{Si} - \right]_2 \text{Cl} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	178.0	16.0	184	24
1,7-Dichloro-1,1,3,3,5,5,7,7-octamethyltetrasiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{ClSi} - \left[\text{O} - \text{Si} - \right]_3 \text{Cl} \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	216.0	10.0	222	15
Residue	—	—	9.0	—	2

reaction proceeds by stagewise condensation with formation of chloroalkylsiloxanes having 2-5 silicon atoms in the molecule.

In the condensation of 2 molecules of dichloromethylsilane with 1 mole of chloroethoxydimethylsilane, new compounds were isolated; their properties are given in Table 3.

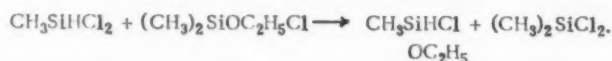
TABLE 2

Substance	Formula	B.p. in °C (p in mm)	M.p. (°C)*	d_{20}^{20}	Yield (%)
1,3-Dichloro-1,1-diethyl-3,3-dimethyldisiloxane	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{CH}_3 \\ \quad \\ \text{ClSi} - \text{O} - \text{SiCl} \\ \quad \\ \text{C}_2\text{H}_5 \quad \text{CH}_3 \end{array}$	77 (18)	-107	1.0299	14.0
1,5-Dichloro-1,1-diethyl-3,3,5,5-tetramethyltrisiloxane	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{CH}_3 \\ \quad \\ \text{ClSi} - \left[\text{O} - \text{Si} - \right]_2 \text{Cl} \\ \quad \quad \\ \text{C}_2\text{H}_5 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	106 (18)	-103	1.0197	13.7
1,7-Dichloro-1,1-diethyl-3,3,5,5,7,7-hexamethyltetrasiloxane	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{CH}_3 \\ \quad \\ \text{ClSi} - \left[\text{O} - \text{Si} - \right]_3 \text{Cl} \\ \quad \quad \quad \\ \text{C}_2\text{H}_5 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	130-133 (18)	-95	1.0158	5.0

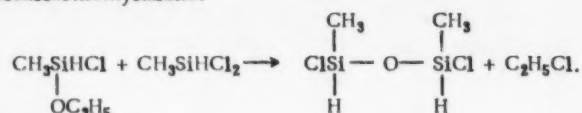
*Melting points are given accurately within $\pm 2^\circ$.

Among the reaction products from the condensation of dichloromethylsilane with chloroethoxydimethylsilane we isolated 19.8% (on the weight of reaction mixture) of dichlorodimethylsilane, which was not a component of the original reaction mixture, and also three compounds containing the grouping $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{Si} - \text{O} - \text{Si} - \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$.

The formation of such compounds is to be explained by the use of an alkylhalosilane containing silicon-attached hydrogen; in presence of ferric chloride disproportionation readily occurs according to the scheme:



The resulting extremely reactive chloroethoxymethylsilane (we did not succeed in isolating it) rapidly condenses with the original dichloromethylsilane:



This side reaction results in the formation of the compounds indicated.

TABLE 3

Substance	Formula	B.p. (°C at 747 mm)	M.p. (°C)	d_{20}^{20}	Yield (%)
1,3-Dichloro-1,3-dimethylsiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{ClSi} - \text{O} - \text{SiCl} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{array}$	103	-128	1.0835	18.3
1,3-Dichloro-1,1,3-trimethylsiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{ClSi} - \text{O} - \text{SiCl} \\ \quad \quad \\ \text{CH}_3 \quad \text{H} \end{array}$	120	-120	1.0609	10.0
1,5-Dichloro-1,3,5-trimethyltrisiloxane	$\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ \quad \quad \quad \\ \text{ClSi} - \left[\text{O} - \text{Si} - \right] \text{Cl} \\ \quad \quad \quad \\ \text{H} \quad \quad \quad \text{H} \end{array} \quad]_2$	148	-112	1.0585	6.4
1,5-Dichloro-1,1,3,5-tetramethyltrisiloxane	$\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ \quad \quad \quad \\ \text{ClSi} - \left[\text{O} - \text{Si} - \right] \text{Cl} \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \text{H} \end{array} \quad]_2$	159	-111	1.0515	2.2

TABLE 4

Substance	Formula	B.p. in °C (p in mm)	M.p. (°C)	d_{20}^{20}	Yield (%)
1,3-Dichloro-3-ethyl-1,1-dimethyldisiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{C}_2\text{H}_5 \\ \quad \quad \\ \text{ClSi} - \text{O} - \text{SiCl} \\ \quad \quad \\ \text{CH}_3 \quad \text{H} \end{array}$	74 (70)	-110	1.0519	7.7
1,3-Dichloro-1,3-diethylsiloxane	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \quad \\ \text{ClSi} - \text{O} - \text{SiCl} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{array}$	81-82 (70)	-128	1.0609	8.1
1,5-Dichloro-3,5-diethyl-1,1-dimethyltrisiloxane	$\begin{array}{c} \text{CH}_3 \quad \quad \text{C}_2\text{H}_5 \\ \quad \quad \quad \\ \text{ClSi} - \left[\text{O} - \text{Si} - \right] \text{Cl} \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \text{H} \end{array} \quad]_2$	81,5-82 (12)	-108	1.0355	8.8
1,5-Dichloro-1,3,5-triethyltrisiloxane	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \quad \text{C}_2\text{H}_5 \\ \quad \quad \quad \\ \text{ClSi} - \left[\text{O} - \text{Si} - \right] \text{Cl} \\ \quad \quad \quad \\ \text{H} \quad \quad \quad \text{H} \end{array} \quad]_2$	89-90 (12)	-111	1.0453	3.3

Disproportionation with formation of chloroethoxyethylsilane proceeds in addition to the main condensation reaction also in the case of the condensation of dichloroethylsilane with chloroethoxydimethylsilane.

This is confirmed by the identities of the new compounds obtained; their properties are given in Table 4.

A study was made of the chlorination of the alkylchlorosiloxanes containing silicon-attached hydrogen which we had synthesized; it was found that this hydrogen is readily replaced by chlorine. The resulting compounds and their properties are given in Table 5.

TABLE 5

Substance	Formula	B.p. in °C (p in mm)	M.p. (°C)	d_{20}^{20}	Yield (%)
1,1,3,3-Tetrachloro- 1,3-dimethyldisiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{ClSi} - \text{O} - \text{SiCl} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	141 (750)	-22	1.3021	88
1,1,3-Trichloro-1,3,3-tri- methyldisiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{ClSi} - \text{O} - \text{SiCl} \\ \quad \\ \text{CH}_3 \quad \text{Cl} \end{array}$	151 (750)	-29	1.1803	82
1,1,3-Trichloro-1-ethyl- 3,3-dimethyldisiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{ClSi} - \text{O} - \text{SiCl} \\ \quad \\ \text{CH}_3 \quad \text{Cl} \end{array}$	58 (7)	-85	1.2233	73
1,1,3,3-Tetrachloro- 1,3-diethyldisiloxane	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{ClSi} - \text{O} - \text{SiCl} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	94 (8)	-60	1.4009	66
1,1,3,5-Tetrachloro- 1,3-diethyl-5,5-di- methyltrisiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{ClSi} - \left[\text{O} - \text{Si} - \right] \text{Cl} \\ \quad \quad \\ \text{CH}_3 \quad \text{Cl} \quad \text{Cl} \end{array}$	110 (7)	-58	1.3290	75
1,1,3,5,5-Pentachloro- 1,3,5-triethyltrisiloxane	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{ClSi} - \left[\text{O} - \text{Si} - \right] \text{Cl} \\ \quad \quad \\ \text{Cl} \quad \text{Cl} \quad \text{Cl} \end{array} \quad]_2$	110 (3)	-36	1.4626	80

EXPERIMENTAL

Preparation of Chloroethoxydimethylsilane. A flask fitted with hermetically sealed stirrer, thermometer, and separating funnel contained 360 g (2.8 moles) of dichlorodimethylsilane, 55.30% Cl, calculated 54.98% Cl, and 128 g (2.8 moles) of ethanol was added from the dropping funnel. The reaction mixture was heated at 80° and then fractionated through a 17-plate column. The product, amounting to 252 g (65.5%), was $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)\text{Cl}$, b.p. 94-95° (745 mm), 25.60% Cl (calculated 25.62% Cl), 32.40% OC_2H_5 (calculated 32.50% OC_2H_5).

Preparation of Alkylchlorosiloxanes. The other reactants were: $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$, 45.19% Cl (calculated 45.16% Cl); $(\text{CH}_3)_2\text{SiCl}_2$, 55.30% Cl (calculated 54.98% Cl), $\text{CH}_3\text{SiHCl}_2$, 61.70% Cl (calculated 61.66% Cl); $\text{C}_2\text{H}_5\text{SiHCl}_2$, 54.91% Cl (calculated 54.96% Cl). The reactions were carried out by the same procedure and in the same apparatus as in the case of the preparation of chloroethoxydimethylsilane, the reactants and 0.5% of FeCl_3 being entered simultaneously into the flask. When reaction was complete, the reaction mixture was filtered from FeCl_3 and rapidly vacuum-distilled from a Wurtz flask. The distillate was fractionated through a 10- or 17-plate column.

The condensation of dichlorodimethylsilane (1 mole, 129 g) with chloroethoxydimethylsilane (1 mole, 138.5 g) was carried out at 50-60°. The condensation products obtained (200 g) were fractionated (the yields are given in Table 1); 51 g of ethyl chloride was also obtained. The residue in the still contained 14.69% Cl

TABLE 6

Substance	Molecular weight		% Cl		% C		% H		% Si		% H (-Si)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1,3-Dichloro-1,3-dimethyl-disiloxane	177	175	40.68	40.50	13.72	13.71	4.55	4.57	32.55	32.09	1.15	1.14
1,3-Dichloro-1,1,3-trimethyl-disiloxane	189	189	37.95	37.60	—	—	—	—	29.91	29.70	0.54	0.53
1,5-Dichloro-1,3,5-trimethyl-trisiloxane	230	234	29.84	29.80	15.12	15.30	5.64	5.13	35.83	35.85	1.20	1.23
1,5-Dichloro-1,1,3,4-tetramethyltrisiloxane	247	249	28.40	28.58	—	—	—	—	34.11	33.84	0.80	0.80
1,3-Dichloro-1,1-diethyl-3,3-dimethyldisiloxane	238	231	29.60	30.75	29.84	31.19	7.39	6.94	25.00	24.23	—	—
1,5-Dichloro-1,1-diethyl-3,3,5,5-tetramethyltrisiloxane	299	305	23.40	23.29	31.81	31.49	7.15	7.21	27.76	27.52	—	—
1,7-Dichloro-1,1-diethyl-3,3,5,5,7,7-hexamethyltetrasiloxane	371	379	19.02	18.73	30.98	31.68	6.77	7.39	29.77	29.51	—	—
1,3-Dichloro-3-ethyl-1,1-dimethyldisiloxane	197	203	35.45	35.00	24.62	23.63	5.95	5.92	27.30	27.60	0.48	0.49
1,3-Dichloro-1,3-diethyldisiloxane	201	203	35.00	35.00	—	—	—	—	27.49	27.60	1.10	0.98
1,5-Dichloro-3,5-diethyl-1,1-dimethyltrisiloxane	268	277	25.75	25.62	25.71	26.01	6.64	6.50	29.55	30.32	0.75	0.72
1,5-Dichloro-1,3,5-triethyltrisiloxane	276	277	25.56	25.62	25.83	26.01	6.40	6.50	30.88	30.32	1.06	1.08

and was evidently a mixture of penta- (calculated 16.67% Cl) and hexasiloxanes (calculated 14.32% Cl) of this series. The condensation of dichlorodiethylsilane with chloroethoxydimethylsilane was carried out at a molar ratio of 2 : 1 at 73-79°. Condensation products from two experiments, amounting to 398 g, were fractionated (the yields are given in Table 2).

The condensation of dichloromethylsilane with chloroethoxydimethylsilane was carried out at a molar ratio 2 : 1 at 48-50°. The condensation products from five experiments, amounting to 1340 g, were fractionated (the yields are given in Table 3). The condensation of dichloroethylsilane with chloroethoxydimethylsilane was carried out at a molar ratio of 2 : 1 at 58-60°. The condensation products from two experiments, amounting to 677 g, were fractionated (the yields are given in Table 4).

Alkylchlorosiloxanes were chlorinated according to the previously described procedure [4] in a glass apparatus cooled with water. Compounds containing only methyl radicals were first diluted with an equal amount of carbon tetrachloride; compounds containing ethyl radicals, or both ethyl and methyl radicals, were chlorinated directly.

The amount of substance taken for chlorination was 10-17 g, the reaction temperature was 11-38°, and the duration of reaction 50-120 minutes. The chlorination products were distilled. The yields obtained after distillation are given in Table 6.

1,1,3,3-Tetrachloro-1,3-dimethyldisiloxane: found Cl 58.56%, Si 23.41%, calculated Cl 58.11%; Si 23.00%. 1,1,3-Trichloro-1,3,3-trimethyldisiloxane: found Cl 46.51%; Si 24.89%; calculated Cl 47.58%; Si 25.12%. 1,1,3-Trichloro-1-ethyl-3,3-dimethyldisiloxane: found Cl 44.64%; Si 22.46%; calculated Cl 44.88%; Si 23.58%. 1,1,3,3-Tetrachloro-1,3-diethyldisiloxane: found Cl 52.01%; calculated 52.25%. 1,1,3,5-Tetrachloro-1,3-diethyl-5,5-dimethyltrisiloxane: found Cl 40.38%; calculated 41.04%. 1,1,3,5,5-Pentachloro-1,3,5-triethyltrisiloxane: found Cl 45.80%; calculated 46.60%.

SUMMARY

1. A study was made of the condensation of chloroethoxydimethylsilane with dichlorodimethylsilane, with dichloromethylsilane, with dichlorodiethylsilane, and with dichloroethylsilane.
2. It was found that this reaction proceeds by stepwise condensation and is a convenient method for the preparation of chloroalkylsiloxanes of low molecular weight.
3. Eleven new intermediate products in the condensation reaction (alkylchlorosiloxanes) and six chlorination products of these were isolated.

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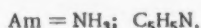
* Original Russian pagination. See C. B. Translation.

ORGANOBORON COMPOUNDS

COMMUNICATION 17. REACTION OF AMINE COMPLEXES OF DIARYLBORINIC ESTERS WITH AROMATIC ORGANOLITHIUM COMPOUNDS. SYNTHESIS OF UNSYMMETRICAL TRIARYLBORINES

B. M. Mikhailov and V. A. Vaver

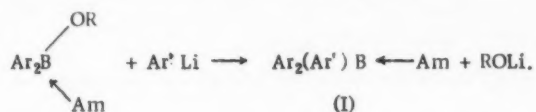
In a previous investigation [1] we showed that treatment of diarylboric esters with aryllithiums results in the formation of complex compounds of the type $[\text{Ar}_2(\text{Ar}')\text{B}(\text{OR})]\text{Li}$. However, when we treated these complex compounds with dry hydrogen chloride, we succeeded in obtaining only the original diarylboric esters. It was further found that these lithium alkoxytriarylborates are decomposed by ammonia or pyridine with displacement of alkoxy from the complex and formation of an ammonia or amine complex of an unsymmetrical triarylborine:



This reaction is analogous to the well-studied transformations of complex compounds of heavy metals, e.g., the transformation of potassium tetrachloroplatinate (II) into dichlorodiammineplatinum:



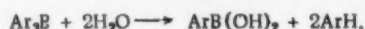
It was mentioned also that amine complexes of triarylborines can be obtained by the action of aryllithiums on amine complexes of diarylboric esters in accordance with the equation:



The present investigation is a more detailed study of the reaction between amine complexes of diarylboric esters and aryllithiums and also the conversion of amine complexes of triarylborines into the triarylborines themselves. Whereas diarylboric esters react very vigorously with organolithium compounds at temperatures from -5° to -20° owing to their exceptionally high tendency to form complexes [2, 3], the reactivity of their amine complexes toward aryllithiums is much lower. Thus, though reaction does occur between aryllithiums and pyridine complexes of diarylboric esters at room temperature, for completion of reaction it is necessary to boil the ethereal reaction mixture for 3–5 hours. Under these conditions, conversion of the amine complexes of diarylboric esters into unsymmetrical triarylborines proceeds very smoothly, so that the reaction products can be isolated in the pure state in high yield. The isolation of the reaction products is extremely simple because all amine complexes of triarylborines are insoluble in water and aqueous alcohol and can be readily separated from lithium alkoxides. In this way we prepared the pyridine complexes of diphenyl-*o*-tolyl-, diphenyl-*p*-tolyl-, and 1-naphthyldiphenyl-borines (I. $\text{Ar} = \text{C}_6\text{H}_5$; $\text{Ar}' = \text{o-CH}_3\text{C}_6\text{H}_4$; $\text{p-CH}_3\text{C}_6\text{H}_4$; $1-\text{C}_{10}\text{H}_7$; $\text{Am} = \text{C}_5\text{H}_5\text{N}$); the pyridine complexes of di-1-naphthylphenyl- and di-1-naphthyl-*o*-tolyl-borines (I. $\text{Ar} = 1-\text{C}_{10}\text{H}_7$; $\text{Ar}' = \text{C}_6\text{H}_5$; $\text{o-CH}_3\text{C}_6\text{H}_4$; $\text{Am} = \text{C}_5\text{H}_5\text{N}$); the pyridine complex of bis-*p*-bromophenyl-*o*-tolylborine (I. $\text{Ar} = \text{p-BrC}_6\text{H}_4$; $\text{Ar}' = \text{o-CH}_3\text{C}_6\text{H}_4$; $\text{Am} = \text{C}_5\text{H}_5\text{N}$); and the ammonia

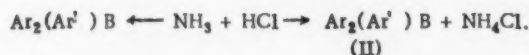
complexes of diphenyl-*p*-tolyl- and bis-*p*-chlorophenylphenylborines I. $\text{Ar}=\text{C}_6\text{H}_5$; $\text{p-ClC}_6\text{H}_4$; $\text{Ar}'=\text{p-CH}_3\text{C}_6\text{H}_4$; C_6H_5 ; $\text{Am}=\text{NH}_3$).

The ready accessibility of the amine complexes still does not solve the question of the synthesis of unsymmetrical triarylborines completely. At first sight the simplest method of isolating triarylborines from their amine complexes would appear to be treatment of their aqueous solutions with a strong mineral acid, but this method has a very serious disadvantage which greatly restricts and generally excludes its application: unsymmetrical triarylborines react fairly rapidly with water, especially in presence of traces of acids, with elimination of one or two aryl radicals:



This reaction, which has been studied by Wittig and coworkers [4] and Neu [5] for triphenylborine, occurs also with other triarylborines. Even when the reaction products are treated very rapidly, much of the triarylborine is broken down. It was found to be impossible to use nonaqueous solutions of organic acids for the isolation of triarylborines because even the strongest of these acids do not react with pyridine complexes. Of the organic acids that we tried (acetic, chloroacetic, trichloroacetic, picric, and oxalic), the only exception was picric acid, which reacted quantitatively with the pyridine complexes of di-1-naphthylphenyl- and di-1-naphthyl-*o*-tolyl- borines with formation of pyridine picrate, but did not react with the pyridine complexes of diphenyl-*o*-tolyl-, diphenyl-*p*-tolyl-, and 1-naphthyl-diphenyl-borines. Isolation of triarylborine by decomposition of the pyridine complexes with picric acid was rendered difficult by the contamination of the product with picric acid and small amounts of pyridine picrate. When attempts were made to distill such a product, explosive decomposition occurred. In this case, however, the triarylborine can be purified chromatographically on alumina.

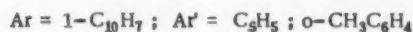
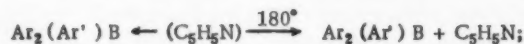
It was hoped that the most universal method of isolating triarylborines from their ammonia and amine complexes would be treatment in an anhydrous solvent with dry hydrogen chloride. It was found in fact that the decomposition of ammonia complexes of triarylborines in ether with dry hydrogen chloride proceeds in accordance with the equation:



Isolation of the triarylborines was not difficult, for ammonium chloride could be filtered off and the solvent could be partially or completely removed under reduced pressure at room temperature. The purity of a triarylborine obtained in this way, with careful manipulation in an atmosphere of nitrogen, is determined only by the purity of the original ammonia complex. In this way we prepared triphenylborine and diphenyl-*p*-tolylborine (II. $\text{Ar}=\text{C}_6\text{H}_5$; $\text{Ar}'=\text{C}_6\text{H}_5$; $\text{p-CH}_3\text{C}_6\text{H}_4$).

It was found that decomposition of pyridine complexes of triarylborines with dry hydrogen chloride is complicated by side reactions.

Finally, another possible way of converting amine complexes into unsymmetrical triarylborines consists in their pyrolysis. Thus, the pyridine complexes of di-1-naphthylphenyl- and di-1-naphthyl-*o*-tolyl- borines are fairly smoothly decomposed in a vacuum at 175–185° with formation mainly of pyridine and the unsymmetrical triarylborines:



EXPERIMENTAL

1-Naphthyl-diphenylborine Pyridine Complex. In this reaction we used the crystalline 1-naphthyllithium ether complex prepared by Mikhailov and Chernova's method [6] from butyllithium and 1-bromonaphthalene in ethereal solution. The pyridine complex of isopentyl diphenylborinate was prepared from 10.01 g (0.04 mole) of isopentyl diphenylborinate and 3.14 g (0.04 mole) of pyridine in 10 ml of dry ether. To this solution a suspension of 8.75 g (0.042 mole) of crystalline 1-naphthyllithium ether complex in 50 ml of dry ether was

added without application of cooling. Each portion of 1-naphthyllithium reacted with evolution of heat and immediately went into solution. The ether solution was heated for four hours, washed with water, evaporated under reduced pressure down to one-fifth of the original bulk, and diluted with methanol. The yield of 1-naphthylidiphenylborine pyridine complex was 8.5 g (57.5%); m.p. 175–108° (with decomposition [1]).

Found %: N 3.67; 3.73; B 2.88; 2.92 $C_{27}H_{22}BN$. Calculated %: N 3.77; B 2.91

Diphenyl-p-tolylborine Pyridine Complex. An ethereal solution of 0.03 mole of p-tolylolithium was added to a solution of isobutyl diphenylborinate pyridine complex prepared from 7.15 g (0.03 mole) of isobutyl diphenylborinate and 2.35 g of pyridine in 30 ml of dry ether. The reaction mixture was boiled for three hours, ether was removed under reduced pressure, and the residue was treated with dilute (1 : 1) methanol. The pyridine complex was filtered off and crystallized from aqueous methanol; yield 7.7 g (77%); m.p. 156–158°.

Found %: N 3.85; 4.11; C 85.96; 85.82; H 6.65; 6.57; B 3.34; 3.38 $C_{24}H_{22}BN$. Calculated %: N 4.18; C 85.98; H 6.62; B 3.23

The pyridine complex of diphenyl-p-tolylborine crystallizes from aqueous alcohol in the form of colorless needles, readily soluble in benzene, sparingly soluble in ether and methanol, and insoluble in water.

Diphenyl-o-tolylborine Pyridine Complex. The substances taken for reaction were butyl diphenylborinate (1.01 g, i.e. 0.004 mole), pyridine (0.34 g), and o-tolylolithium (0.005 mole). The reaction mixture was boiled for three hours and washed with water, ether was removed under reduced pressure, and the residue was diluted with aqueous alcohol. Diphenyl-o-tolylborine pyridine complex was filtered off and crystallized from aqueous acetone; yield 1.23 g (87%); m.p. 177–179° [1].

Found %: N 4.09; 4.13; B 3.23; 3.20 $C_{24}H_{22}BN$. Calculated %: N 4.18; B 3.23

The pyridine complex of diphenyl-o-tolylborine is readily soluble in acetone, sparingly soluble in methyl and ethyl alcohols, and insoluble in water.

Di-1-naphthylphenylborine Pyridine Complex. The substances taken for reaction were isobutyl di-1-naphthylborinate (10.1 g, i.e., 0.03 mole), pyridine (2.4 g), and phenyllithium (0.035 mole). The conditions used for the reaction and the isolation of the pyridine complex were the same as in the preceding experiment. The yield of the pyridine complex of di-1-naphthylphenylborine was 11.5 g (91%); m.p. 215–217° (with decomposition [1]).

Found %: N 3.29; 3.36; B 2.52; 2.48 $C_{31}H_{24}BN$. Calculated %: N 3.32; B 2.57

Di-1-naphthyl-o-tolylborine Pyridine Complex. In a similar way, from 5.1 g (0.015 mole) of isobutyl di-1-naphthylborinate, 1.28 g of pyridine, and 0.0153 mole of o-tolylolithium we obtained 5.05 g (77%) of di-1-naphthyl-o-tolylborine pyridine complex, m.p. 203–205° [1], undepressed by admixture of an analyzed sample of di-1-naphthyl-o-tolylborine pyridine complex.

Bis-p-bromophenyl-o-tolylborine Pyridine Complex. The substances taken for reaction were isobutyl bis-p-bromophenylborinate (1.97 g, i.e., 5 mmoles) [3], 0.39 g of pyridine, and 5 mmoles of o-tolylolithium. After being boiled for three hours, the ethereal solution of reaction products was washed with water and ether was removed under reduced pressure. The residue was diluted with 10 ml of 90% methanol. The pyridine complex of bis-p-bromophenyl-o-tolylborine was filtered off and crystallized from aqueous methanol; yield 1.5 g (72%).

Found %: B 2.20; 2.23; N 2.37; 2.51 $C_{24}H_{20}BBr_2N$. Calculated %: B 2.19; N 2.48

The pyridine complex of bis-p-bromophenyl-o-tolylborine is a colorless crystalline substance, readily soluble in acetone, methanol, and ethanol, but insoluble in water.

Diphenyl-p-tolylborine Ammonia Complex. A solution of 0.03 mole of p-tolylolithium was added to a vigorously stirred suspension of 6.04 g (0.024 mole) of isobutyl diphenylborinate ammonia complex* in 30 ml of dry ether, no cooling being applied. The reaction mixture was boiled for four hours and then treated first with gaseous ammonia and then with water. The ether layer was separated and evaporated under reduced pressure; the residue was diluted with 15 ml of water and 5 ml of methanol. The ammonia complex of diphenyl-p-tolylborine was prepared by passing ammonia through an isopentane solution of the diphenylborinic ester.

-p-tolylborine was filtered off, washed with water, dried, and recrystallized from dry benzene; yield 3.40 g (53%). When heated in a capillary, the ammonia complex sintered at 140–150° and melted with decomposition at 189–191°.

Found %: N 5.04; 5.00; B 3.94; 3.97 $C_{19}H_{20}BN$. Calculated %: N 5.13; B 3.96

Diphenyl-p-tolylborine ammonia complex crystallizes from benzene in the form of colorless crystals, readily soluble in acetone, sparingly soluble in cold benzene, and insoluble in petroleum ether.

Bis-p-chlorophenylphenylborine Ammonia Complex. The substances taken for reaction were isobutyl bis-p-chlorophenylborinate ammonia complex (8.0 g, i.e., 0.025 mole) and phenyllithium (0.025 mole). The synthesis and isolation of the ammonia complex of bis-p-chlorophenylphenylborine were carried out under the same conditions as those of the ammonia complex of diphenyl-p-tolylborine. The yield was 3.7 g (42.5%); m.p. 213–215° after recrystallization from alcohol.

Found %: C 66.47; 66.22; H 5.16; 5.17; B 3.26; 3.53; N 4.44; 4.36; $C_{18}H_{16}BNCl_2$. Calculated %: C 65.90; H 4.92; B 3.30; N 4.27.

Bis-p-chlorophenylphenylborine ammonia complex is readily soluble in methyl and ethyl alcohols, but insoluble in water.

Diphenyl-p-tolylborine. Diphenyl-p-tolylborine was prepared by treating its pyridine complex with 30% sulfuric acid. The reaction was carried out in a small three-necked flask fitted with a sealed high-speed stirrer, dropping funnel, and tube for passage of nitrogen. The pyridine complex of diphenyl-p-tolylborine (3.2 g, i.e., 0.01 mole) and 20 ml of ether were introduced into the nitrogen-filled apparatus, the stirrer was switched on, and 15 ml of 30% sulfuric acid was added rapidly to the suspension. After five minutes of vigorous stirring, the pyridine complex had gone completely into solution. The ether layer was rapidly separated and dried with potassium carbonate. Ether was removed, and vacuum distillation of the residue in a stream of nitrogen gave 1.25 g (49%) of diphenyl-p-tolylborine, b.p. 170–173° (3 mm).

Found %: B 4.19; 4.20 $C_{19}H_{17}B$. Calculated %: B 4.22

When cooled diphenyl-p-tolylborine solidified to a colorless crystalline mass, readily soluble in most organic solvents. Diphenyl-p-tolylborine was obtained also by the decomposition of its ammonia complex with dry hydrogen chloride.

Decomposition of Diphenyl-p-tolylborine Ammonia Complex with Dry Hydrogen Chloride. An ethereal solution of hydrogen chloride (12 ml, 0.48 g/ml, i.e., 0.016 mole) was added to a solution of 3.81 g (0.014 mole) of diphenyl-p-tolylborine ammonia complex in 5 ml of dry acetone. Ammonium chloride (0.6 g; theory requires 0.73 g) was filtered off, and, after removal of solvents, the ethereal solution yielded 2.88 g of diphenyl-p-tolylborine, b.p. 171–172° (3 mm).

Pyrolysis of Di-1-naphthylphenylborine Pyridine Complex. Di-1-naphthylphenylborine. The pyrolysis was carried out in a small vacuum-distillation flask with a low side tube leading to a pear-shaped receiver. The flask was heated in a metal bath. A trap for pyridine, cooled during the experiment with a mixture of solid carbon dioxide and ether, was placed between the apparatus and the vacuum pump. The pyridine complex (5.94 g, i.e., 0.014 mole) was placed in the flask, the apparatus was evacuated, and the bath was heated to 175–185°. The pyridine complex melted and at the same time vigorous liberation of pyridine vapor began; it stopped after 10–15 minutes, and the trap containing pyridine was removed. The yield of pyridine was 0.98 g (87.5%). The liquid residue was distilled rapidly under a reduced pressure of nitrogen, and it gave 0.5 g of naphthalene, m.p. 79–80° (after recrystallization from alcohol) and 2.2 g of a fraction of b.p. 230–240° (2 mm), which solidified to a glassy mass on cooling. Recrystallization of the main fraction from a mixture of benzene and petroleum ether gave 1.84 g (45%) of di-1-naphthylphenylborine, m.p. 146–148° (in a sealed capillary in an atmosphere of nitrogen).

Found %: C 91.59; 91.42; H 5.81; 5.81; B 3.08; 3.18 $C_{26}H_{19}B$. Calculated %: C 91.25; H 5.59; B 3.16

Di-1-naphthylphenylborine is a colorless crystalline substance, readily soluble in benzene, but sparingly in petroleum ether.

Pyrolysis of Di-1-naphthyl-o-tolylborine Pyridine Complex. Di-1-naphthyl-o-tolylborine. The pyrolysis was carried out under the same conditions and in the same apparatus as in the case of the di-1-naphthylphenylborine pyridine complex. The amount of the pyridine complex taken was 4.5 g (0.01 moles). The products were 0.70 g (88.5%) of pyridine and 2.89 g of a fraction of b.p. 243–249° (3.5 mm). Redistilla-

tion of the main fraction gave 2.10 g of di-1-naphthyl-o-tolylborine, b.p. 197-199° (0.08 mm).

Found %: C 90.88; 90.82; H 5.94; 5.96; B 3.24; 3.09 $C_{27}H_{21}B$. Calculated %: C 91.02; H 5.94; B 3.04

Di-1-naphthyl-o-tolylborine is a slightly yellowish viscous substance which solidifies to a glassy mass when cooled. It is readily soluble in benzene and dichloroethane, but insoluble in petroleum ether and isopentane.

Decomposition of Triphenylborine Ammonia Complex with Dry Hydrogen Chloride. Triphenylborine ammonia complex (0.96 g, i.e., 3.7 mmoles) was dissolved in 3 ml of dry acetone. Dry ether (5 ml) and ethereal hydrogen chloride (3 ml, 0.048 g/ml; i.e., 4 mmoles) were added to the solution. The precipitate of ammonium chloride was filtered off and washed with ether (amount obtained 0.17 g; theory requires 0.02 g). The filtrate was evaporated down to 2-2.5 ml and diluted with a 3 : 1 mixture of petroleum ether and diethyl ether. The product (0.47 g) was triphenylborine, m.p. 136-138° [7]. Excess of solvent was again removed from the filtrate, and a further 0.1 g of triphenylborine, m.p. 130-135°, was isolated. The total yield was 0.57 g (62.5%).

Decomposition of Di-1-naphthyl-o-tolylborine Pyridine Complex with Picric Acid. A solution was prepared by heating 3.74 g (8.6 mmoles) of di-1-naphthyl-o-tolylborine pyridine complex with 80 ml of dry benzene, and a solution of 1.96 g of picric acid in 20 ml of dry benzene was added. Pyridine picrate was filtered off, washed with a little benzene, and vacuum-dried. The pyridine picrate amounted to 2.4 g (95.5%) and melted at 162-164°. After recrystallization from alcohol the picrate melted at 165-166° and showed no depression in a mixture test with a known sample of the picrate. The benzene solution containing di-1-naphthyl-o-tolylborine, a little pyridine picrate, and some picric acid was passed through a 15 x 150 mm column of alumina, after which elution was effected with 50 ml of a 1 : 1 ether-benzene mixture. Solvents were removed, and vacuum distillation of the residue gave 2.5 g (82%) of di-1-naphthyl-o-tolylborine, b.p. 196-199° (0.08 mm).

Found %: B 3.07; 3.05 $C_{27}H_{21}B$. Calculated %: B 3.04

SUMMARY

1. Treatment of aryllithiums with ammonia and amine complexes of diarylborinic esters gave the corresponding complexes of triarylborines. In this way several ammonia and pyridine complexes of unsymmetrical triarylborines were prepared.
2. Ammonia and amine complexes of triarylborines can be converted into the triarylborines themselves by the action of mineral acids, picric acid, dry hydrogen chloride, and also by pyrolysis.

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* Original Russian pagination. See C.B. Translation.

1. The first part of the report is a general introduction to the subject of the study. It discusses the importance of the study and the objectives of the research. It also provides a brief overview of the methodology used in the study.

2. The second part of the report is a detailed description of the study area. It includes information about the location of the study area, the population of the study area, and the characteristics of the study area. It also discusses the data sources used in the study.

3. The third part of the report is a detailed description of the study results. It includes information about the findings of the study, the conclusions drawn from the findings, and the implications of the findings. It also discusses the limitations of the study and the need for further research.

CONDENSATION OF TRICHLOROMETHYLSILANE IN SILENT DISCHARGES

COMMUNICATION 2

D. N. Andreev

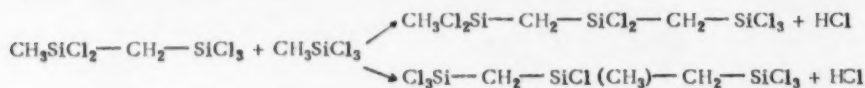
In the first communication [1] we showed that, under the action of silent discharges, trichloromethylsilane undergoes condensation, and about one half of the condensate formed consists of compounds obtained by the condensation of two CH_3SiCl_3 molecules. Two previously underscribed organosilicon compounds were isolated from the condensation products: 1,1,1,3,3-pentachloro-1,3-disilabutane and 1,1,1,4,4-pentachloro-1,4-disilapentane, amounting to 17% and 10% respectively of the condensate. The first of these compounds was later described by Sadykh-Zade, Chernyshev, and Mironov [2], who isolated it from direct synthesis products obtained by passing $(\text{CH}_3)_2\text{Cl}_2\text{SiCH}_2\text{Cl}$ over silicon-copper alloy at 370–400°.

The condensation of trichloromethylsilane in silent discharges is accompanied by the formation of a little acetylene, which indicates partial rupture of the $\text{Si}-\text{CH}_3$ bond, which is energetically least stable in comparison with the other bonds ($\text{Si}-\text{Cl}$ and $\text{C}-\text{H}$) present in the CH_3SiCl_3 molecule. The formation of $\cdot\text{CH}_3$ and $\cdot\text{SiCl}_3$ radicals as the result of rupture of this bond gave grounds for the view that the condensation process must proceed by a chain mechanism in which these radicals and also hydrogen atoms formed by the conversion of methyl radicals into acetylene take part. A chain mechanism for the condensation is indicated also by the formation of high-boiling chloromethylsilanes which, it is suggested, contain compounds of composition $\text{R}_3-4\text{Cl}_6-7\text{Si}_3$ (in which $\text{R} = \text{CH}_2$ or CH_3).

The present paper gives the results of a further investigation of the composition of the condensate obtained from CH_3SiCl_3 and describes the apparatus in which the condensation experiments were carried out. In view of the fact that investigation of the composition and structure of polychloromethylsilanes is considerably complicated by the high hydrolyzability of these compounds, individual fractions of our condensate were exhaustively methylated or ethylated by the action of methyl- or ethyl-magnesium halides and the corresponding methyl or ethyl derivatives so obtained were investigated. Ethylation of light fractions of the condensate (b.p. 120–160°) gave some tetraethylsilane, which indicates that these fractions contained hexachlorodisilane. The degrading effect of various Grignard reagents on hexachlorodisilane has been noted previously by various investigators. In particular, it was shown that in reaction between $\text{Cl}_3\text{SiSiCl}_3$ and ethylmagnesium bromide, not only hexamethyldisilane, but also tetraethylsilane was formed [3]. In the investigation of the methylation products obtained from the high-boiling fractions of the condensate (b.p. 100–200° (4 mm)), we isolated 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane $[(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{CH}_2-\text{Si}(\text{CH}_3)_3]$ and 2,2,4,4,7,7-hexamethyl-2,4,7-trisilaoctane $[(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{CH}_2-\text{Si}(\text{CH}_3)_3]$.

The formation of the first of these compounds in the methylation of Fraction I' of b.p. 104–112° (4 mm) indicates that it contains a polychloromethylsilane having the grouping $\equiv \text{Si}-\text{CH}_2-\text{Si}-\text{CH}_2-\text{Si} \equiv$ in the main chain. The silicon and chlorine contents of this fraction indicate that the compound is of composition $\text{C}_3\text{H}_7\text{Cl}_7\text{Si}_3$, i.e., that it should contain one methyl side group. Two structural isomers are possible for polychloromethylsilanes of this composition: $\text{Cl}_3\text{Si}-\text{CH}_2-\text{SiCl}_2-\text{CH}_2-\text{SiCl}_2(\text{CH}_3)$ and $\text{Cl}_3\text{Si}-\text{CH}_2-\text{SiCl}(\text{CH}_3)-\text{CH}_2-\text{SiCl}_3$, both of which would give the same 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane when methylated. It is therefore very difficult to establish which of these isomers is present in this fraction of polychloromethylsilanes. It is possible

that both are present, particularly as they could be formed equally readily by chain processes from 1,1,1,3,3-pentachloro-1,3-disilabutane:



In the methylation of Fractions II* and III*, b.p. 130–150° and 150–200° (4 mm), we isolated 2,2,4,4,7,7-hexamethyl-2,4,7-trisilaoctane $[(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{CH}_2-\text{Si}(\text{CH}_3)_3]$. The formation of this compound indicates that the original fractions contained polychloromethylsilanes containing the grouping $\equiv \text{Si}-\text{CH}_2-\text{CH}_2-\text{Si} \equiv$ in the main chain.

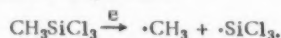
The chlorine and silicon contents of these fractions indicate that the polychloromethylsilanes must have the composition $\text{C}_4\text{H}_9\text{Cl}_7\text{Si}_3$, i.e., must contain one methyl side group attached to one of the silicon atoms. Three isomeric structures are possible for compounds of the composition indicated: $(\text{CH}_3)_2\text{Cl}_2\text{Si}-\text{CH}_2-\text{CH}_2-\text{SiCl}_2-\text{CH}_2-\text{SiCl}_3$; $\text{Cl}_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{SiCl}(\text{CH}_3)-\text{CH}_2-\text{SiCl}_3$, and $\text{Cl}_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{SiCl}_2-\text{CH}_2-\text{SiCl}_2(\text{CH}_3)$.

All these would give 2,2,4,4,7,7-hexamethyl-2,4,7-trisilaoctane when methylated. It did not appear to be possible to establish by the usual methods of chemical investigation which of these isomeric polychloromethylsilanes were formed in the condensation process. We can be sure only that these isomers of composition $\text{C}_4\text{H}_9\text{Cl}_7\text{Si}_3$ were formed by further transformation of the primarily formed dimers, 1,1,1,3,3-pentachloro-1,3-disilabutane and 1,1,1,4,4-pentachloro-1,4-disilapentane. It is most probable that they are formed from the second compound $(\text{CH}_3-\text{SiCl}_2-\text{CH}_2-\text{CH}_2-\text{SiCl}_3)$, which contains the grouping $\equiv \text{Si}-\text{CH}_2-\text{CH}_2-\text{Si} \equiv$, in its main chain.

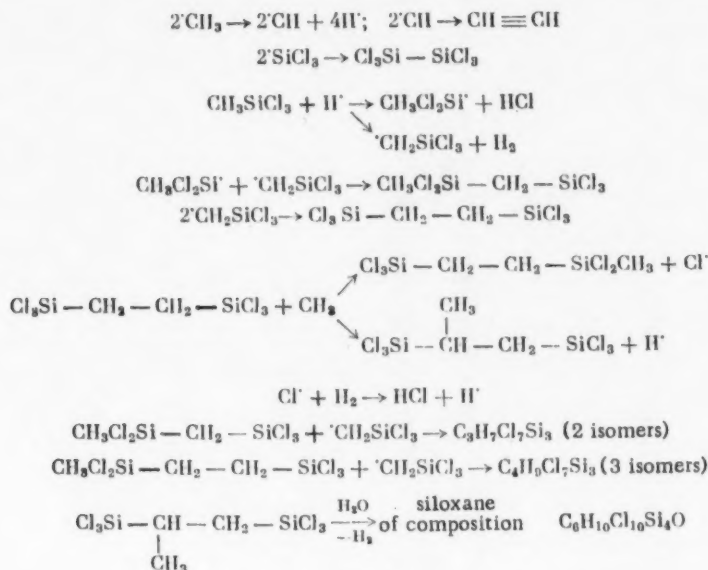
By exhaustive methylation of the solid residue remaining after vacuum distillation of liquid polychloromethylsilanes, we isolated an organosilicon compound which, according to its elementary analysis and physicochemical constants, corresponded to a siloxane of composition $\text{C}_{16}\text{H}_{40}\text{Si}_4\text{O}$. This substance decolorized bromine water, but gave a negative reaction for monosubstituted acetylenic hydrocarbons. The C/H ratio indicates that the molecule should contain one double bond, and the C/Si ratio indicates (even if we assume that the compound contains the grouping $\equiv \text{Si}-\text{CH}_2-\text{CH}_2-\text{Si} \equiv$ in the main chain) that there is an excess of two carbon atoms as compared with the siloxane containing four silicon atoms $[(\text{CH}_3)_2\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{O}-(\text{CH}_3)_2\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{CH}_3)_3]$ and having the composition $\text{C}_{14}\text{H}_{38}\text{Si}_4\text{O}$. From all this it follows that the siloxane of composition $\text{C}_{16}\text{H}_{40}\text{Si}_4\text{O}$ (and also the polychloromethylsilane from which this siloxane was formed by partial hydrolysis) should contain the grouping $\equiv \text{Si}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{Si} \equiv$ in the main chain.

The formation of a methyl group as a side chain to the ethylene bridge $(-\text{CH}_2-\text{CH}_2-)$ could be the result of methylation at a C—H bond occurring in chain reactions in which $\cdot\text{CH}_3$ radicals formed in the breakdown of the CH_3SiCl_3 molecule take part. The possibility of methylation, and also alkylation and arylation, of chloromethylsilanes at Si—Cl bonds was proved by us previously [1,4], and the possibility of the formation of new C—C bonds in organosilicon compounds was established in our first communication [1] for the case of the formation of 1,1,1,4,4-pentachloro-1,4-disilapentane $(\text{CH}_3-\text{SiCl}_2-\text{CH}_2-\text{CH}_2-\text{SiCl}_3)$ from CH_3SiCl_3 . As regards the route by which the unsaturated siloxane $(\text{C}_6\text{H}_{10}\text{Cl}_{10}\text{Si}_4\text{O})$ was formed, there can be no doubt that it was obtained as a result of side and secondary reactions, partial hydrolysis of polychloromethylsilanes (by traces of moisture that found its way into the reactor), and subsequent dehydrogenation of the siloxane formed. It is probable that siloxanes containing conjugated double bonds were formed, for after two months' standing some of the fractions of the methylation products gelled as a result of autopolymerization.

The isolation of three more individual organosilicon compounds made it possible to correct and somewhat extend the previously proposed [1] scheme for the mechanism of the condensation process. The primary reaction is rupture of the Si—C bond of trichloromethylsilane:



All subsequent reactions proceed by a chain mechanism with participation of free atoms and radicals:



Thus, the investigation has shown that, in silent discharges (24.5 kv, 2.25 ma, and 50 cycles per second), polychloromethylsilanes containing alternating silicon and carbon atoms can be synthesized from trichloromethylsilane. The main condensation products are polychloromethylsilanes corresponding in composition to $\text{C}_{2-3}\text{H}_{5-7}\text{Cl}_5\text{Si}_2$ and $\text{C}_{3-4}\text{H}_{7-9}\text{Cl}_7\text{Si}_3$, formed by the condensation of two or three CH_3SiCl_3 molecules. The content of these compounds in the condensate was 60% by weight.

EXPERIMENTAL

Description of Apparatus. The experiments on the effect of silent discharges on trichloromethylsilane were carried out in the apparatus shown diagrammatically in Figure 1. In the glass reactor 1, the water jacket a served as one electrode and the glass tube b as the other. A glass rod was sealed to the end of this tube, and at the end of this were three welded thickenings for the purpose of centering the internal electrode b. The jacket a and tube b were filled with sodium chloride solution, and aluminum-wire electrodes were passed into these. The internal electrode b was connected to one terminal of a high-voltage transformer, and the external electrode a and the other terminal of the transformer were earthed. The discharge occurred in the annular space (5 mm thick, 300 mm high) between the external surface of the internal electrode b, diameter 10 mm, and the internal surface c of the external electrode a, diameter 20 mm. The round-bottomed flask 2, capacity 300–350 ml, contained the organosilicon compound; 3 is an electric air bath; the spiral traps 4 are connected in series and cooled in Dewar vessels to a temperature of from -30° to -50° ; the two spiral condensers 5 are cooled with water mains; the drying column 6 contains phosphoric oxide on pumice; the wash bottle 7 contains concentrated sulfuric acid; the gas filter 8 has a sealed-in porous glass diaphragm; 9 is a calcium chloride tube; the U-tube 10 is filled with glass wool and phosphoric oxide.

The hydrogen used in the experiments was taken from cylinders, and before it entered the discharge tube it was first purified by passage through a solution of potassium dichromate in sulfuric acid, through a porcelain tube filled with copper turnings and heated to 700° , and through columns containing solid potassium hydroxide, calcium chloride, and phosphoric oxide. The parts of the apparatus were connected together with the aid of rubber stoppers and flexible polyvinyl chloride tubing. The joints were smeared on the outside with Mendelev grease.

Experimental Procedure. Before an experiment, in order to remove traces of moisture from the apparatus, the heater for the flask was switched on and dry hydrogen was passed through the apparatus for $2\frac{1}{2}$ –3 hours.

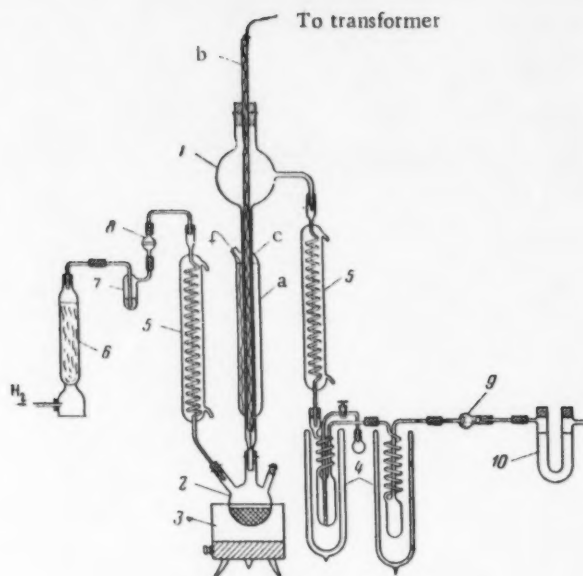


Fig. 1

When the flask was cool, the organosilicon compound under investigation was introduced through a side tube, the heater was switched on, and hydrogen was again passed to displace air. In order to prevent entry of air due to reduction of pressure, passage of hydrogen was stopped only after the apparatus had cooled completely.

In the experiments, the heater for the flask was first switched on and at the same time passage of hydrogen was started. Hydrogen was passed at an average rate of 0.7-1.0 liter/hour. Heating of the flask was regulated so that the rate at which liquid flowed from the discharge tube into the flask did not exceed 2-3 drops per second. The high tension was switched on after uniform boiling of the liquid had been established. At the end of the experiment the heater was switched off, but the hydrogen stream was turned off only when the apparatus was completely cold.

The voltage of the primary circuit was measured by an ASTV astatic voltmeter of the 0.5 class, and the current by an AST astatic ammeter of the 0.5 class. The voltage of the secondary circuit was measured by an S-96 kilovoltmeter of the 1.5 class, and the current by an AVO-5 ampere-voltmeter.

Experiments with Trichloromethylsilane. The trichloromethylsilane used in the experiments had b.p. 65° and contained 70.5-71% of hydrolyzable chlorine. In order to establish the experimental conditions necessary for the production of acceptable yields of condensation products, a series of experiments at different voltages was carried out. The best results were obtained at a primary p.d. of 90 v (1.8-1.9 amp), corresponding to a secondary 24.5 kv* and 2.25 ma; the frequency was 50 cycles per second. Attempts to determine the composition of the outgoing gases (with respect to hydrocarbon components) by the usual adsorption method did not give satisfactory results owing to the negligible content of unsaturated hydrocarbons in the gases. In all experiments a qualitative test with Ilosvay's reagent showed that acetylene was formed. A special experiment was carried out to determine acetylene quantitatively.

Experiment 1. The flask contained 190 g (1.27 moles) of CH_3SiCl_3 . The primary tension was 90 v, and the secondary was 24.5 kv; the duration of the experiment was 10 hours. After being passed through two spiral traps (-50° to -30°), the outgoing gases passed successively through wash bottles containing strong KOH solution, dilute HCl, Ilosvay's solution (two bottles), dilute HCl, bromine water, and KOH solution. The precipitate of copper acetylide was dissolved in acidified ferric sulfate solution, and acetylene was determined by titration with 0.1 N KMnO_4 . The amount of acetylene found was 84.5 mg (0.00325 mole). No gaseous olefins were detected in the outgoing gas.

*Direct measurements showed that the tension in the secondary circuit was not 27 kv, as stated previously [1], but 24.5 kv.

In order to obtain a sufficiently large amount of condensation products, four experiments were carried out under the same conditions of electric discharge with 808 g of CH_3SiCl_3 in all and a total reaction time of 191 hours. After two fractionations through a 12-15-plate column apart from unchanged trichloromethylsilane, we obtained the following fractions:

Fr. I, B.p.	100—120°; 3,5 g	Fr. II, B.p.	120—140°; 6,0 g;
Fr. III, B.p.	140—150°; 3,5 g	Fr. IV, B.p.	150—160°; 6,5 g;
	(21,42; 21,30% Si; 65,9% Cl)	Fr. V, B.p.	160—170°; 2,0 g;
Fr. VI, B.p.	170—180°; 8,0; (21,26; 21,29% Si; 67,4; 66,9% Cl)		
Fr. VII, B.p.	180—190°; 45,0g	Fr. VIII, B.p.	190—210°; 26,0g.

The last two fractions were fractionated further and, as a result, the following two compounds were isolated:

1,1,1,3,3-Pentachloro-1,3-disilabutane $[(\text{CH}_3)_2\text{SiCl}_2-\text{CH}_2-\text{SiCl}_3]$; b.p. 182–185°; 26 g.

Found %: Si 21.34; 21.88; Cl 67.1; 66.9 $\text{C}_2\text{H}_5\text{Cl}_5\text{Si}_2$. Calculated %: Si 21.38; Cl 67.54

The literature [2] gives b.p. 183.5–184.5°.

1,1,1,4,4-Pentachloro-1,4-disilapentane $[(\text{CH}_3)_2\text{SiCl}_2-\text{CH}_2-\text{CH}_2-\text{SiCl}_3]$; b.p. 199–203°; 13 g.

Found %: Si 20.32; 20.58; Cl 64.3 $\text{C}_3\text{H}_7\text{Cl}_5\text{Si}_2$. Calculated %: Si 20.29; Cl 64.12

Raman spectrum (intensities on relative scale given in parentheses): 127 cm^{-1} (1); 153 cm^{-1} (1); 198 cm^{-1} (1); 202 cm^{-1} (2); 295 cm^{-1} (10); 465 cm^{-1} (8); 695 cm^{-1} (3); 765 cm^{-1} (3); 1262 cm^{-1} (9); 1401 cm^{-1} (9); 2906 cm^{-1} (15); 2984 cm^{-1} (15). When cooled, this substance and the neighboring fraction of b.p. 195–199° solidified and then had m.p. $\sim 5^\circ$.

By vacuum fractionation (4–5 mm) in a stream of dry air we isolated the following fractions:

Fr. I', B.p.	104—112°; 35 g (23,13; 23,11% Si; 63,8; 63,5% Cl)
Fr. II', B.p.	130—150°; 20 g (22,41; 22,51% Si; 62,8% Cl)
Fr. III', B.p.	150—200°; 17 g (22,64; 22,99% Si; 63,8; 63,4% Cl)
Fr. IV', residue, B.p.	$> 200^\circ$

The residue (Fraction IV'), a dark-colored solid resin, amounted to 60 g.

Fractions I' and II' were clear colorless liquids, and Fraction III' was a rather viscous clear colorless liquid. All these compounds hydrolyzed rapidly in moist air. In order to establish the composition and structure of the polychloromethylsilanes contained in the condensate, individual fractions of the condensate were converted into methyl and ethyl derivatives by treatment with excess of methyl- and ethyl-magnesium halides, and these products were investigated.

Investigation of Fractions II, III, and IV, b.p. 120–140°, 140–150°, and 150–160°. An ethereal solution of 14 g of combined Fractions II, III, and IV was added to the Grignard reagent obtained from 1 mole of magnesium and 1.1 moles of ethyl bromide in 300 ml of dry ether. The mixture was heated for five hours, most of the ether was distilled off, and the reaction mixture was heated further for three days. After the decomposition treatment and removal of ether, the reaction products were fractionated and gave 2.7 g of tetraethylsilane, b.p. 154–157°; n_D^{20} 1.4278; d_4^{20} 0.7650; Found MR 48.5; Calculated 48.8; For $(\text{C}_2\text{H}_5)_4\text{Si}$ the literature [6] gives: 153°; n_D^{20} 1.4268; d_4^{20} 0.7662.

Investigation of Fraction I', b.p. 104–112° (4 mm). An ethereal solution of 30 g of the fraction was added to the Grignard reagent prepared from 1.5 moles of magnesium and methyl iodide in 350 ml of dry ether. The mixture was heated for three hours, most of the ether was distilled off, and the reaction mixture was heated further for four hours. After the decomposition treatment and removal of ether we obtained 19.5 g of liquid, fractionation of which through a small column gave 4.1 g of a substance having b.p. 204–210°; n_D^{20} 1.4461; d_4^{20} 0.8018; M 224, Found MR 77.37; Calculated [5] 77.32.

Found %: Si 35.94; 35.89; C 51.89; 52.06; H 12.09; 12.15 $\text{C}_{10}\text{H}_{28}\text{Si}_3$. Calculated %: Si 36.22; C 51.64; H 12.13

For 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane the literature [7] gives: b.p. 206°; n_D^{20} 1.4420; d_4^{20} 0.7987. The substance isolated was therefore 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane.

Investigation of Fractions II', b.p. 130–150° (4 mm), and III', b.p. 150–200° (4 mm). An ethereal solution of combined Fractions II' and III' (33 g) was added to the Grignard reagent prepared from 61 g (2.5 moles) of magnesium and methyl bromide in 700 ml of dry ether. The mixture was heated for three hours, ether was distilled off, 200 ml of dry toluene was added, and the reaction mixture was heated further for four hours. After the decomposition treatment and removal of ether and toluene, 10.5 g of methylation products was obtained. Fractionation through a small column gave 3.9 g of a substance having b.p. 87–92° (10 mm); n_D^{20} 1.4470; d_4^{20} 0.8051; Found MR 81.84; Calculated [5] 81.95

Found %: Si 34.02; 34.19; C 53.95; 53.69; H 12.07 $C_{11}H_{30}Si_3$. Calculated %: Si 34.16; C 53.57; H 12.26

The compound isolated was therefore 2,2,4,4,7,7-hexamethyl-2,4,7-trisilaoctane.

Investigation of the Solid Residue IV' of Polychloromethylsilanes, b.p. > 200° (4 mm). An ethereal solution of 60 g of the solid residue was added to the Grignard reagent prepared from 97 g (4 moles) of magnesium and methyl bromide in 750 ml of dry ether. The mixture was heated for eight hours, most of the ether was distilled off, and the reaction mixture was heated in a water bath for two days. After the decomposition treatment and removal of ether, we obtained 32.5 g of methylation products, from which 11 g of a liquid boiling up to 230° (15 mm) was isolated by vacuum fractionation. The residue was 20.5 g of a solid resin. Vacuum fractionation of the liquid methylation products gave 4.2 g of a substance of b.p. 175–190° (8 mm), which had a sharp unpleasant odor, rapidly decolorized bromine water, but gave a negative reaction with Ilosvay's reagent for monosubstituted acetylenic compounds; b.p. 175–180° (8 mm); n_D^{20} 1.4768; d_4^{20} 0.8886; Found M 354; 344; Found MR 114.67; Calculated M 360.8; MR 114.01.

Found %: Si 31.66; 31.56; C 53.49; 53.66; H 11.10; 11.21; $C_{16}H_{40}Si_4O$. Calculated %: Si 31.13; C 53.26; H 11.18

The neighboring fraction, b.p. 150–175° (8 mm), had the same chemical properties and similar constants (n_D^{20} 1.4740; d_4^{20} 0.8723) and elementary composition (32.04–32.18% Si; 53.31–53.74% C; and 11.36–11.39% H). When kept for two months, the residue from the fractionation was converted into a clear gel.

The Raman spectrum was determined by V. A. Kolesova, to whom we express our deep gratitude.

SUMMARY

1. It was shown that, under the action of silent discharges, trichloromethylsilane undergoes condensation and gives a mixture of polychloromethylsilanes in a yield of about 50%. The main reaction products are compounds formed by the condensation of two or three CH_3SiCl_3 molecules.
2. We established the presence of the following compounds among the condensation products: 1,1,1,3,3-pentachloro-1,3-disilabutane, 1,1,1,4,4-pentachloro-1,4-disilapentane, and mixtures of isomers of polychloromethylsilanes of composition $C_3H_7Cl_7Si_3$ and $C_4H_9Cl_7Si_4$. As a result of the methylation of these last compounds we isolated 2,2,4,4,6,6-hexamethyl-2,4,6-trisilahelptane and 2,2,4,4,7,7-hexamethyl-2,4,7-trisilaoctane.
3. It was shown that the primary reaction is the rupture of the Si—C bond of trichloromethylsilane and formation of free $\cdot CH_3$ and $\cdot SiCl_3$ radicals. A reaction mechanism is proposed on the basis of chain processes proceeding with participation of free radicals and hydrogen atoms.
4. As a result of this work it has been shown that it is possible to prepare polychloromethylsilanes containing alternating silicon and carbon atoms in the main chain with the aid of silent discharges.

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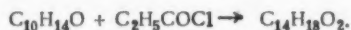
SYNTHESIS AND POLYMERIZATION OF p-tert-BUTYLPHENYL METHACRYLATE

COMMUNICATION 1

M. M. Koton, T. V. Sheremetyeva, and M. G. Zhenevskaya

In recent years methacrylic esters have aroused ever-increasing interest, both practical and theoretical. Many papers [1] have been devoted to the elucidation of the relation between the structures and properties of these esters and their polymers. In these investigations a fairly detailed study of alkyl methacrylates and their derivatives has been made, but there is scarcely any information in the literature about aryl methacrylates. This information is confined to the review article published by the firm of du Pont [2] in 1936, in which the constants of phenyl and o-tolyl methacrylate monomers and the softening points of their polymers are given.

In order to make up partially for this deficiency, we synthesized and characterized the previously undescribed p-tert-butylphenyl methacrylate (p-tert-BPM), which was prepared in the usual way by reaction between p-tert-butylphenol and methacryloyl chloride:



p-tert-BPM is a crystalline substance, readily soluble in ether, acetone, benzene, chloroform, and hot alcohol, but insoluble in water; m.p. 34.5–35°; b.p. 131–132° (4 mm).

Found %: C 77.25; H 7.87 Calculated %: C 77.06; H 8.32

Bromine value: found 72.72; calculated 73.25

p-tert-BPM readily polymerizes. Polymerization was carried out in sealed tubes in an atmosphere of nitrogen in presence of benzoyl peroxide (0.1, 0.5, 1, and 5% on the weight of monomer) in an air thermostat with stage-wise rise of temperature. The polymerization schedule was as follows: 24 hours at 60°, 24 hours at 80°, 24 hours at 100°, and 24 hours at 120°.

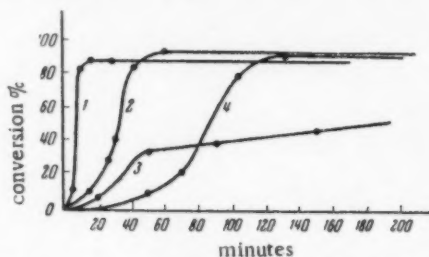
No.	Amount of initiator (% by weight)	Conversion (%)	Intrinsic viscosity
1	0.1	85.7	2.5
2	0.5	90.6	2.25
3	1.0	88.4	0.6
4	5.0	88.5	0.58

p-tert-BPM polymer is a transparent glassy substance. In all experiments we determined the percent conversion – the polymer being precipitated from acetone solution with alcohol and then dried to constant weight – and the intrinsic viscosity of the reprecipitated polymer. In the table we give results for individual experiments.

The results show that the intrinsic viscosity, and therefore the average molecular weight, diminishes by a factor of more than four with increase in the amount of initiator, and the percent conversion does not exceed 90. Hence, not less than 10% of the monomer remains either unchanged or in the form of polymerization products of low molecular weight. Comparative experiments were carried out on the rates of polymerization of p-tert-BPM and of methyl methacrylate (MMA) at 70° and 100°. The results of the experiments are shown in the graph.

It will be seen from the graph that at 100° the polymerization of p-tert-BPM is considerably more rapid than that of MMA. Thus, in 15 minutes the conversion attains 89% and then remains constant. At 70° the

polymerization of *p*-tert-BPM is at first much greater than that of MMA, but when the conversion attains 40% the rate of polymerization falls and becomes less than that of MMA. We consider that this fall in the rate of polymerization at a comparatively low conversion (40%) of *p*-tert-BPM and also the large amount of residual monomer in the final mass-polymerization product may be explained by the presence of a branched substituent in the benzene nucleus and the consequent steric hindrance. With rise in the viscosity of the polymerizate, diffusion of monomer into the polymer-monomer aggregate becomes more difficult and the probability of collisions between the monomer and the macroradicals of growing polymer chains becomes lower, which results in reduction in the rate of polymerization.



Rates of polymerization: 1) BPM solution, 100°; 2) MMA, 100°; 3) BPM solution, 70°; 4) MMA, 70°.

SUMMARY

1. Previously-undescribed *p*-tert-butylphenyl methacrylate was synthesized and characterized.
2. It was shown that the mass polymerization of this ester at 60–120° with benzoyl peroxide as initiator proceeds to the extent of 89–90%.
3. It was suggested that the large amount of residual monomer in the final product is to be explained by the presence of a branched substituent in the benzene nucleus and the consequent steric hindrance.

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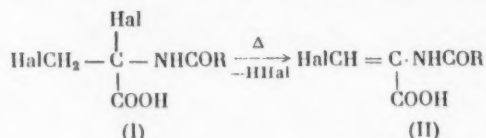
Received May 5, 1956

2-ACYLAMINO-3-HALOACRYLIC ACIDS

COMMUNICATION 2. REACTIONS WITH AMINES AND THIOLS: NEW METHOD OF PREPARING DERIVATIVES OF PENALDIC ACIDS

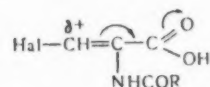
O. V. Kildisheva, M. G. Linkova, S. S. Talts, and I. L. Knunyants

We showed previously [1] • that N-acyl-2,3-dihaloalanines (I), heated in inert solvents in absence of moisture, readily lose hydrogen halide with formation of 2-acylamino-3-haloacrylic acids (II):

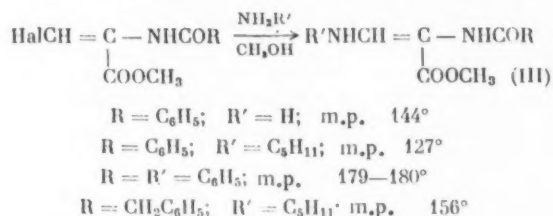


Further investigations showed that the most characteristic property of 2-acylamino-3-haloacrylic acids is the high mobility of the halogen atom, which is analogous to the mobility of halogen in 2-chlorovinyl ketones [2]. Thus, treatment with nucleophilic reagents such as amines and mercaptans results in replacement of halogen and formation of the corresponding derivatives of acrylic acid.

The readiness with which 2-acylamino-3-haloacrylic acids react with nucleophilic reagents can be explained by the powerful electrophilic character of the β -carbon atom arising from conjugation in the acrylic system:

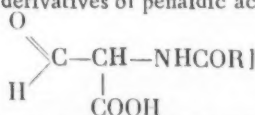


Thus, by the action of bases such as ammonia, aniline, and piperidine on 2-acylamino-3-haloacrylic esters in an alcohol medium we obtained 2-acylamino-3-amino (or arylamino) acrylic esters (tautomeric forms of Schiff bases) (III):



The resulting compounds are derivatives of penaldic acids (acylaminomalonaldehydic acids) and were found

[α -formyl-N-acylglycine

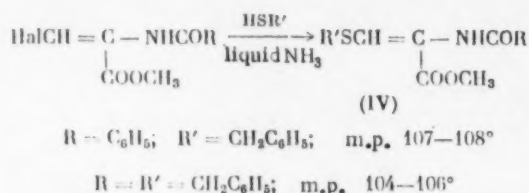


to be identical with compounds prepared previously

• Communication 6, printed in this Journal, 1955, p. 282 (C.B. Translation p. 251), will be treated as Communication 1 in this series of investigations.

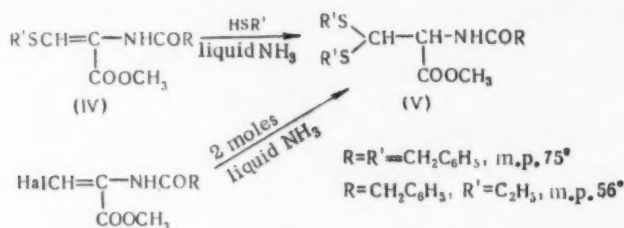
by the condensation of aniline or piperidine with difficultly accessible acetals of penaldic esters [3].

By the action of thiols (ethane- and α -toluene-thiols) on solutions of 2-acylamino-3-haloacrylic esters in liquid ammonia we obtained 2-acylamino-3-(alkylthio) acrylic esters (IV) in high yields:

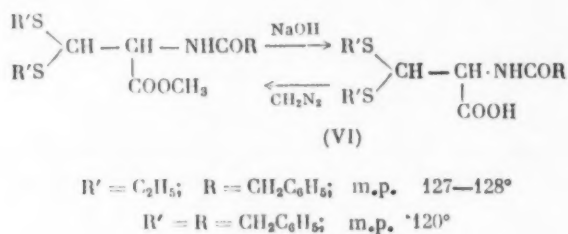


Unlike their esters and amides, 2-acylamino-3-haloacrylic acids combine with thiols with some considerable difficulty, which finds its natural explanation in the lower electrophilic character of the β -carbon atom of acrylic acids, as compared with their esters.

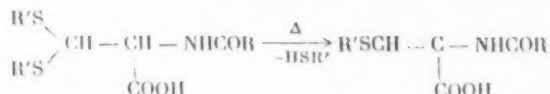
The presence of a vinyl sulfide grouping in (IV) was confirmed by the addition of a second thiol molecule with formation of thioacetals of penaldic esters (V):



The same thioacetals were obtained directly by the action of excess (2 molecular proportions) of alkanethiol on 2-acylamino-3-haloacrylic esters. The resulting thioacetals of penaldic esters (V) were readily hydrolyzed to the corresponding acids (VI), which were reconverted into the original esters (V) by treatment with diazomethane:



The acid (VI) ($\text{R} = \text{C}_2\text{H}_5$; $\text{R}' = \text{CH}_2\text{C}_6\text{H}_5$) was prepared previously by condensation of ethanethiol with penaldic ester [4]. The thioacetals of the acids (VI) were found to be rather unstable compounds: when heated they readily lost a thiol molecule with formation of 2-acylamino-3-(alkylthio)acrylic acids (VII):



EXPERIMENTAL

Methyl 3-Amino-2-benzamidoacrylate (III) ($R = C_6H_5$; $R' = H$)

Methyl 2-benzamido-3-chloroacrylate was prepared by the scission of 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one by means of methanol. A mixture of 2 g (0.01 mole) of the oxazolinone and 3 ml of absolute methanol was prepared, and one drop of 10% potassium carbonate solution or sodium methoxide solution was added. After ten minutes all had gone into solution and reaction for oxazolinone was negative. The alcohol was removed in a vacuum, and the residue was crystallized from diethyl ether or petroleum ether. The product, obtained in quantitative yield, was methyl 2-benzamido-3-chloroacrylate, m.p. 92-93°, undepressed by admixture of a sample prepared by treatment of 2-benzamido-3-chloroacrylic acid with diazomethane. A mixture of 0.48 g (0.002 mole) of methyl 2-benzamido-3-chloroacrylate and 5 ml of 12% methanolic ammonia was left for two days at room temperature. Alcohol was removed in a vacuum, and the residue was crystallized from water or alcohol. The product, amounting to 0.3 g, was methyl 3-amino-2-benzamidoacrylate, m.p. 144° (from alcohol).

Found %: C 59.72; H 5.47; N 12.75; $C_{11}H_{12}O_3N_2$. Calculated %: C 60.00; H 5.45; N 12.72

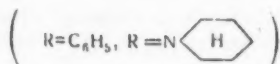
The ester obtained was dissolved in 2 N HCl; with 2,4-dinitrophenylhydrazine it gave a hydrazone of m.p. 190-191° (from glacial acetic acid), identical with the 2,4-dinitrophenylhydrazone of the methyl ester of benzamidomalonaldehydic acid [5].

Found %: N 17.2 $C_{17}H_{15}O_7N_5$. Calculated %: N 17.4

Methyl 3-Anilino-2-benzamidoacrylate (III) ($R = R' = C_6H_5$)

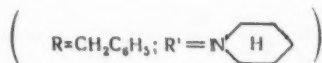
A solution of 0.24 g (0.001 mole) of methyl 2-benzamido-3-chloroacrylate in 3 ml of absolute methanol was treated with a solution of 0.18 g (0.002 mole) of aniline in 2 ml of absolute methanol. On the next day the alcohol was removed in a vacuum, and the residue was crystallized from alcohol. The product, amounting to 0.15 g, was methyl 3-anilino-2-benzamidoacrylate, m.p. 179°, undepressed by admixture of a sample prepared by scission of 4-(anilinomethylene)-2-phenyl-2-oxazolin-5-one with methanol in presence of sodium methoxide [6].

Methyl 2-Benzamido-3-piperidinoacrylate (III)



A solution of 0.24 g (0.001 mole) of methyl 2-benzamido-3-chloroacrylate in 3 ml of absolute methanol was mixed with 0.17 g (0.002 mole) of piperidine. After one hour the alcohol was removed in a vacuum and the crystalline residue was washed with water. The product, amounting to 0.2 g, was methyl 2-benzamido-3-piperidinoacrylate, m.p. 127° (from alcohol by addition of water until crystallization began), undepressed by admixture of a sample obtained by the action of piperidine on the methyl ester of benzamidomalonaldehydic acid. Methyl 2-benzamido-3-piperidinoacrylate is soluble in 2 N HCl, and with 2,4-dinitrophenylhydrazine it gives a 2,4-dinitrophenylhydrazone identical with that obtained from the methyl ester of benzamidomalonaldehydic acid [5].

Methyl 2-(2-Phenylacetamido)-3-piperidinoacrylate (III)



Piperidine (0.17 g, i.e., 0.002 mole) was added to 0.3 g (0.001 mole) of methyl 3-bromo-2-(2-phenylacetamido)acrylate in 3 ml of absolute methanol. The product, amounting to 0.26 g, was methyl 2-(2-phenyl-

acetamido)-3-piperidinoacrylate, m.p. 156° (from a mixture of methanol and ether), undepressed by admixture of a sample prepared by the action of piperidine on the methyl ester of (2-phenylacetamido)malonaldehydic acid.

Methyl 2-Benzamido-3-(benzylthio)acrylate (IV) ($R = C_6H_5$; $R' = CH_2C_6H_5$)

α -Toluenethiol (0.16 g, i.e., 0.0013 mole) was added to a solution of 0.3 g (0.0012 mole) of methyl 2-benzamido-3-chloroacrylate in liquid ammonia. After two days the ammonia was allowed to evaporate and the residue was washed with water. The product, amounting to 0.3 g (75%), was methyl 2-benzamido-3-(benzylthio)acrylate, m.p. 107-108° (from ethyl acetate).

Found %: C 65.78; H 5.17; S 9.62; N 4.08 $C_{18}H_{17}O_3NS$. Calculated %: C 66.06; H 5.20; S 9.8; N 4.28

2-Benzamido-3-(benzylthio)acrylanilide

2-Benzamido-3-chloroacrylanilide (0.51 g, i.e., 0.0017 mole) and α -toluenethiol (0.3 g, i.e., 0.0024 mole) were added to a solution 0.12 g of potassium amide in liquid ammonia. After two days the ammonia was allowed to evaporate and the residue was washed with water and ether. The product, amounting to 0.5 g (78%), was 2-benzamido-3-(benzylthio)acrylanilide, m.p. 191-192° (from methanol).

Found %: C 71.11; H 5.29; S 8.11; N 6.89; $C_{23}H_{17}O_3NS$. Calculated %: C 71.13; H 5.16; S 8.22; N 7.21

2-Benzamido-3-chloroacrylanilide

A solution of 0.2 g of 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one in 5 ml of dry ether was treated with a solution of 0.18 ml of acetic acid and 0.2 ml of aniline in 2 ml of dry ether. After 30-40 minutes the precipitate formed was filtered off, washed with water and crystallized from chloroform. The product, amounting to 0.13 g (46%), was 2-benzamido-3-chloroacrylanilide, m.p. 195-196°.

Found %: C 63.07; H 4.65; N 9.57; Cl 12.88; $C_{16}H_{12}O_2N_2Cl$. Calculated %: C 63.89; H 4.33; N 9.32; Cl 11.81

2-Benzamido-3-(benzylthio)acrylic Acid

α -Toluenethiol (0.3 g, i.e., 0.0024 mole) was added to a solution of 0.4 g (0.002 mole) of 2-benzamido-3-chloroacrylic acid in liquid ammonia. After two days the ammonia was allowed to evaporate. The residue was dissolved in water, and the alkaline solution was extracted with ether and then acidified with 2 N H_2SO_4 . The product, amounting to 0.07 g (11.3%), was 2-benzamido-3-(benzylthio)acrylic acid, m.p. 204-205° (from absolute alcohol). The melting point of 2-benzamido-3-(benzylthio)acrylic acid obtained previously [7] by the action of α -toluenethiol on 4-(ethoxymethylene)-2-phenyl-2-oxazolin-5-one was 205-206°.

Found %: C 64.76; H 4.93; S 10.15 $C_{17}H_{15}O_3NS$. Calculated %: C 64.76; H 4.76; S 10.22

Methyl 3-(Benzylthio)-2-(2-phenylacetamido)acrylate (IV) ($R=R'=CH_2C_6H_5$)

a) α -Toluenethiol (0.62 g, i.e., 0.005 mole) was added to a solution of 1.5 g (0.005 mole) of methyl 3-bromo-2-(2-phenylacetamido)acrylate in 25 ml of liquid ammonia. After 24 hours the ammonia was allowed to evaporate and the residue was washed with water. The product, obtained in 86% yield, was methyl 3-(benzylthio)-2-(2-phenylacetamido)acrylate, m.p. 104-106° (from ether).

Found %: C 66.83; H 5.93; S 9.33; N 4.24; Calculated %: C 66.86; H 5.57; S 9.38; N 4.10

b) 3-(Benzylthio)-2-(2-phenylacetamido)acrylic acid prepared by hydrolysis of the ester obtained by method (a) was treated with ethereal diazomethane. The methyl ester obtained was identical with the ester obtained by method (a).

3-(Benzylthio)-2-(2-phenylacetamido)acrylic Acid

Methyl 3-(benzylthio)-2-(2-phenylacetamido)acrylate (0.2 g) was mixed with methanol (1.5 ml) and 1 ml of 2 N methanolic NaOH was added. After 24 hours the alcohol was evaporated off at room temperature and the residue was dissolved in 2 ml of water and filtered. Acidification of the filtrate with 2 N H_2SO_4 gave 3-(benzylthio)-2-(2-phenylacetamido)acrylic acid, m.p. 176-178° (from alcohol).

Found %: C 65.39; H 5.32; S 9.74 $C_{18}H_{17}O_3NS$. Calculated %: C 66.05; H 5.20; S 9.8

3,3-Bisbenzylthio-N-(phenylacetyl)alanine Methyl Ester (V) ($R = R' = CH_2C_6H_5$)

a) Methyl 3-bromo-2-(2-phenylacetamido)acrylate (5 g) was dissolved in 25 ml of liquid ammonia, and 4.28 g (2 equivalents) of α -toluenethiol was added. After 24 hours the ammonia was allowed to evaporate and the residue was washed with water. The product, obtained in quantitative yield, was 3,3-bisbenzylthio-N-(phenylacetyl)alanine methyl ester, m.p. 75° (from 50% alcohol or ether).

Found %: C 66.75; H 5.83; S 13.40 $C_{26}H_{27}S_2O_3N$. Calculated %: C 67.09; H 5.81; S 13.75

b) Methyl 3-(benzylthio)-2-(2-phenylacetamido)acrylate (0.1 g) was dissolved in liquid ammonia and treated with α -toluenethiol. The product was 3,3-bisbenzylthio-N-(phenylacetyl)alanine methyl ester, identical with the methyl ester described above.

3,3-Bisethylthio-N-(phenylacetyl)alanine

Methyl 3-bromo-2-(2-phenylacetamido)acrylate (2.2 g) was dissolved in 20 ml of liquid ammonia, and 1 g (2 equivalents) of ethanethiol was added. After 24 hours the ammonia was allowed to evaporate and the residue was treated with ether. The insoluble precipitate was filtered off and washed with water. The product, amounting to 0.18 g, was the amide of 3,3-bisethylthio-N-(phenylacetyl)alanine, m.p. 167-169° (from ethyl acetate).

Found %: C 55.42; H 6.81; S 19.16; N 8.87 $C_{15}H_{22}N_2O_2S_2$. Calculated %: C 55.2; H 6.74; S 19.0; N 8.5

The ethereal solution was evaporated to dryness. The residue (2.4 g) was hydrolyzed with 1 N methanolic NaOH (room temperature, 24 hours). Alcohol was removed, the residue was dissolved in water, and the solution was acidified with 2 N H_2SO_4 . The oily precipitate was extracted with ether. The ether extract was washed twice with saturated $NaHCO_3$ solution. The alkaline solution was acidified with 2 N H_2SO_4 . The product, amounting to 1.8 g, was 3,3-bisethylthio-N-(phenylacetyl)alanine, m.p. 127-128° (from 50% alcohol). The melting point of 3,3-bisethylthio-N-(phenylacetyl)alanine obtained by the action of ethanethiol on the methyl ester of (2-phenylacetamido)malonaldehydic acid was 130-131° [8].

3-(Ethylthio)-2-(2-phenylacetamido)acrylic Acid

3,3-Bisethylthio-N-(phenylacetyl)alanine was heated to 70-80°. 3-(Ethylthio)-2-(2-phenylacetamido)acrylic acid, m.p. 167°, was obtained. The melting point of 2-(ethylthio)-2-(2-phenylacetamido)acrylic acid obtained by hydrolysis of 2-benzyl-4-(ethylthiomethylene)-2-oxazolin-5-one was 167-168° [9].

SUMMARY

It was shown that derivatives of difficultly accessible penaldic acids, in particular Schiff bases and thioacetals of penaldic acids, can be obtained by reaction of 2-acylamino-3-haloacrylic acids with various nucleophilic reagents, such as ammonia, piperidine, aniline, α -toluenethiol, and ethanethiol.

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[8] Ibid., 508 (1949).

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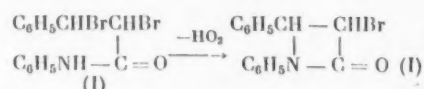
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ISOMERIZATION OF LACTAMS OF β -AMINO ACIDS (2-AZETIDINONES) INTO HYDROCARBOSTYRILS

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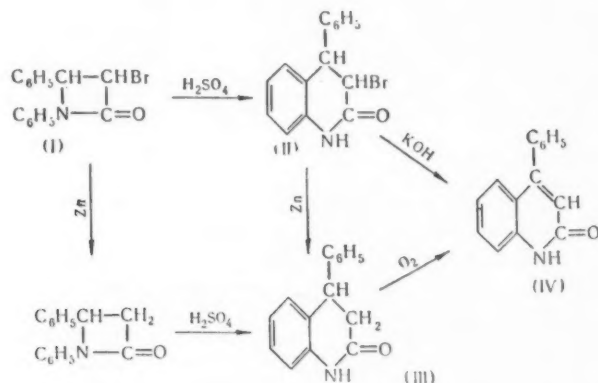
In a previous communication [1] it was shown that substituted amides of β -halohydrocinnamic acid are converted by treatment with potassium or sodium amide in liquid ammonia into the corresponding 2-azetidinones having a 3-substituent that permitted the further introduction of an acylamino group such as is present in the β -lactam part of the penicillin molecule.

The most readily accessible synthesis appeared to be that of 3-bromo-1,4-diphenyl-2-azetidinone (I), which was indeed obtained in almost quantitative yield by treatment of α , β -dibromohydrocinnamanilide with potassamide, sodamide, or sodium hydroxide in liquid ammonia:

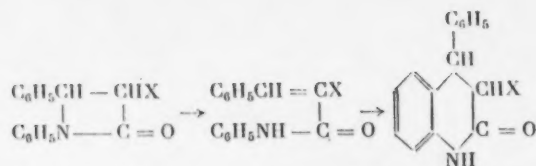


The structure of 3-bromo-1,4-diphenyl-2-azetidinone was proved by its reduction to 1,4-diphenyl-2-azetidinone by long boiling with zinc dust in ethanol. 1,4-Diphenyl-2-azetidinone was found to be exceptionally stable: it remained unchanged after prolonged boiling with concentrated hydrochloric acid or 3 N NaOH and also after treatment with potassamide in liquid ammonia.

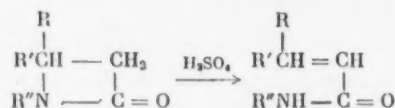
When treated with concentrated sulfuric acid in the cold, 3-bromo-1,4-diphenyl-2-azetidinone undergoes a peculiar change and is isomerized to 3-bromo-4-phenylhydrocarbostyryl (II). 1,4-Diphenyl-2-azetidinone reacts similarly and is isomerized to 4-phenylhydrocarbostyryl (III), identical with the product of the reduction of (II) with zinc dust in ethanol. The structures of (II) and (III) were proved by the formation of the previously described [2] 4-phenylcarbostyryl (IV) by the dehydrobromination of (II) and the oxidation of (III) with chromium trioxide in glacial acetic acid.



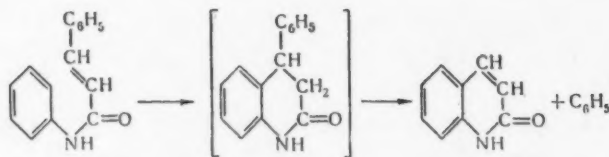
The mechanism of the isomerization can be represented as follows:



We considered that the conversion of β -lactams into amides of unsaturated acids should be quite possible, it being analogous to the well known conversion of β -amino acids into unsaturated acids. The correctness of this view was confirmed for the cases of 1-cyclohexyl-4-phenyl-, 1-benzyl-4-phenyl-, 4-methyl-1-phenyl-, and 4,4-dimethyl-1-phenyl-2-azetidinones, which were converted into amides of the corresponding α , β -unsaturated acids by treatment with concentrated sulfuric acid:



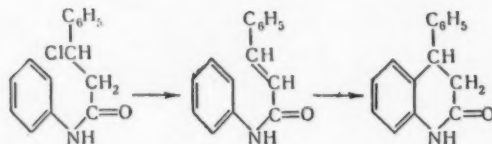
The cyclization arylamides of unsaturated acids has been described for the case of the formation of dimethylhydrocarbostyrils by the treatment of the anilide, *o*- and *p*-toluidides [3], mesitylamide [4] of senecioic acid with aluminum chloride. However, 4-phenylhydrocarbostyrils cannot be obtained in this way because, under these conditions, the anilide and *p*-toluidide of cinnamic acid lose benzene and give carbostyril [3]:



There is also one reference to similar cyclization in presence of concentrated sulfuric acid: when heated with concentrated sulfuric acid, 3,3-diphenylacrylanilide is converted into 4,4-diphenylhydrocarbostyril [5].

Our experiments showed that, under the conditions of the isomerization of 1,4-diphenyl-2-azetidinone in presence of concentrated sulfuric acid in the cold, cinnamanilide is cyclized to 4-phenylhydrocarbostyril in the normal manner, without elimination of benzene. It may be regarded as established, therefore, that the isomerization of β -lactams into substituted hydrocarbostyrils proceeds via the formation of unsaturated amides.

The cyclization of β -chlorohydrocinnamanilide into 4-phenylhydrocarbostyril proceeds by an analogous mechanism:



When β -chlorohydrocinnamanilide is dissolved in concentrated sulfuric acid in the cold, there is vigorous liberation of hydrogen chloride. If the reaction is stopped after 15–20 minutes, then it is possible to isolate cinnamanilide, but if the reaction is continued further 4-phenylhydrocarbostyril is formed. When β -chloro-N-cyclohexylhydrocinnamamide is treated with concentrated sulfuric acid, hydrogen chloride is eliminated much more slowly and N-cyclohexylcinnamamide is formed.

The intermediate formation of the unsaturated amide in the cyclization of β -chlorohydrocinnamanilides to 4-phenylhydrocarbostyrils is apparently specific for cinnamanilides, for, according to Mayer, Zutphen, and Philipps [6], arylamides of 3-chlorobutyric and 3-chloropropionic acids are cyclized directly to substituted

carbostyrils when treated with aluminum chloride.

EXPERIMENTAL

3-Bromo-1,4-diphenyl-2-azetidinone (I)

a) To a solution of 0.82 g (0.02 mole) of sodium hydroxide in liquid ammonia, 7.7 g (0.019 mole) of α, β -dibromohydrocinnamanilide (XIII) was added. On the next day the ammonia was evaporated and the residue washed with water. The product, amounting to 5.8 g (96%), was (I), m.p. 203–204° (from alcohol).

Found %: C 59.86; H 4.86 $C_{15}H_{12}ONBr$. Calculated %: C 59.63; H 4.63

When boiled for 20 hours with zinc dust in alcohol, 3-bromo-1,4-diphenyl-2-azetidinone was converted quantitatively into 1,4-diphenyl-2-azetidinone, m.p. 153–154°, undepressed by admixture of known 1,4-diphenyl-2-azetidinone.

b) To a solution of 0.42 g (0.0075 mole) of potassamide in liquid ammonia, 2.9 g (0.0075 mole) of (XIII) was added. The yield of 3-bromo-1,4-diphenyl-2-azetidinone was 1.95 g (85.5%); with sodamide the yield of (I) was 78.2%.

Unlike substituted amides of β -halohydrocinnamic acid not having a bromine atom in the 3-position, (I) is formed also by treatment of α, β -dibromohydrocinnamanilide with liquid ammonia. A suspension of 0.5 g (0.0165 mole) of (XIII) in liquid ammonia was kept for two weeks with occasional stirring. The product, 0.15 g (38%) of crystals, was identical with (I). When (XIII) was treated with alcoholic potassium or sodium hydroxide, a mixture of cis- and trans- α -bromocinnamic acids was obtained.

4-Methyl-1-phenyl-2-azetidinone (V)

3-Bromobutyranilide was prepared in the usual way from the acid chloride and aniline in ether; yield 87%.

Found %: N 5.78 $C_{10}H_{12}NOBr$. Calculated %: N 5.78

To a solution of 1.15 g (0.029 mole) of sodamide in liquid ammonia, 5.8 g (0.024 mole) of 3-bromobutyranilide was added. On the next day ammonia was evaporated and water was added to the residue. The mixture was extracted with ether. Distillation gave 1 g (26.4%) of (V), b.p. 138–140° (3 mm) and 2.2 g (58%) of crotonanilide.

Found %: N 8.69 $C_{10}H_{11}NO$. Calculated %: N 8.68

4,4-Dimethyl-1-phenyl-2-azetidinone (VI)

3-Bromo-2-methylbutyranilide was prepared from the acid chloride aniline in ether; yield 79%.

Found %: N 5.38 $C_{11}H_{14}NOBr$. Calculated %: N 5.46

3-Bromo-2-methylbutyranilide (1.01 g) was added to a solution of 0.27 g of potassamide in liquid ammonia. After a few hours ammonia was evaporated and the residue was washed, first with water and then with hot heptane. The products were senecianilide, amounting to 0.47 g (68%), and (VI), obtained from the heptane solution; yield 0.19 g (27.5%); m.p. 43–45° (from heptane).

Found %: N 8.04 $C_{11}H_{13}NO$. Calculated %: N 8.00

cis- and trans- α -Bromocinnamanilides (VII) and (VIII)

a) α, β -Dibromohydrocinnamanilide (0.4 g) was added to a solution of 0.1 g of potassium hydroxide in absolute alcohol. After 20 minutes water was added, and fractional crystallization from alcohol gave:

1) 0.25 g (83%) of α -bromocinnamanilide of m.p. 151–152° (VII);

Found %: C 58.71; H 3.93; N 4.53 $C_{15}H_{12}ONBr$. Calculated %: C 59.63; H 3.97; N 4.63

2) 0.036 g (12%) of α -bromocinnamanilide of m.p. 77–78° (VIII); the literature [7] gives m.p. 80° for α -bromocinnamanilide.

Found %: C 59.20; H 4.14 $C_{15}H_{12}ONBr$. Calculated %: C 59.63; H 3.97

b) To a solution of 0.1 g of sodium hydroxide in methanol, 0.4 g of (XIII) was added. After 20 minutes water was added, and fractional crystallization from alcohol gave 0.16 g (53%) of (VII) and 0.14 g (47%) of (VIII).

Isomerization of 1,4-Diphenyl-2-azetidinone into 4-Phenylhydrocarbostyryl (III)

1,4-Diphenyl-2-azetidinone (1 g) was dissolved in 5 ml of concentrated sulfuric acid. On the next day the solution was diluted with water and the precipitated crystals were filtered off. A yield of 0.4 g (40%) of crystals, m.p. 177–178° (from absolute alcohol), was obtained.

Found %: N 6.23 $C_{15}H_{13}ON$. Calculated %: N 6.28

When (III) was oxidized with chromium trioxide in glacial acetic acid, crystals of m.p. 255–256° (from alcohol) were obtained. The literature gives m.p. 259° for 4-phenylcarbostyryl.

Isomerization of 3-Bromo-1,4-diphenyl-2-azetidinone into 3-Bromo-4-phenylhydrocarbostyryl (II)

0.8 g of (I) was dissolved in 5 ml of concentrated sulfuric acid. On the next day the solution was diluted with water, and the crystals precipitated were filtered off. The product, amounting to 0.58 g (72.5%) was 3-bromo-4-phenylhydrocarbostyryl, m.p. 164–165° (from alcohol).

Found %: C 59.10; H 4.11; Br 26.47; N 4.56 $C_{15}H_{12}ONBr$. Calculated %: C 59.63; H 3.97; Br 26.4; N 4.63

Boiling of (II) for 12 hours with zinc dust in ethanol gave crystals of m.p. 177–178°, identical with 4-phenylhydrocarbostyryl (III).

4-Phenylcarbostyryl (IV)

a) A mixture of 0.3 g (0.001 mole) of (II) and 5 ml of 0.5 N alcoholic potassium hydroxide was heated for 30 minutes in a water bath and then diluted with water; the precipitated crystals were filtered off. The product, amounting to 0.2 g (91%), was 4-phenylcarbostyryl, m.p. 257–258° (from alcohol); the literature [2] gives m.p. 259°.

b) Chromium trioxide (0.4 g) was added gradually to a suspension of 0.15 g (0.0005 mole) of (III) in 2 ml of glacial acetic acid. After 20 minutes water was added and the precipitated crystals were filtered off and recrystallized from absolute alcohol. The resulting crystals had m.p. 256–257°, undepressed by admixture of the 4-phenylcarbostyryl obtained by the dehydrobromination of (II).

Cyclization of Cinnamanilide into 4-Phenylhydrocarbostyryl

Cinnamanilide (1 g) was dissolved in 3 ml of concentrated sulfuric acid. On the next day water was added and the precipitate formed was filtered off. The product – 0.4 g (40%) of crystals, m.p. 177–178° – was identical with 4-phenylhydrocarbostyryl.

Cyclization of β -Chlorohydrocinnamanilide

a) β -Chlorohydrocinnamanilide (1 g) was dissolved in 2 ml of concentrated sulfuric acid. After 20 minutes water was added and the crystals formed were filtered off. The product had m.p. 150–151° (from alcohol) and was identical with cinnamanilide.

b) β -Chlorohydrocinnamanilide (2.6 g, i.e., 0.01 mole) was dissolved into 6 ml of concentrated sulfuric acid. There was vigorous liberation of hydrogen chloride. On the next day the mixture was diluted with water and filtered. The product – 0.85 g (38.6%) of crystals, m.p. 177–178° – was identical with 4-phenylhydrocarbostyryl.

N-Cyclohexylcinnamamide (IX)

a) 1-Cyclohexyl-4-phenyl-2-azetidinone (0.1 g) was dissolved in 1 ml of concentrated sulfuric acid. On the next day the solution was diluted with water and the precipitated crystals were filtered off. The product – 0.098 g (98%) of crystals, m.p. 173–174° – was identical with N-cyclohexylcinnamamide.

b) β -Chloro-N-cyclohexylhydrocinnamamide (0.4 g) was dissolved in 2 ml of concentrated sulfuric acid.

After one hour the solution was diluted with water and the precipitated crystals were filtered off. The product - 0.2 g (58%) of crystals, m.p. 171-172° (from alcohol) - was identical with (IX).

Senecianilide (X)

a) 4,4-Dimethyl-1-phenyl-2-azetidinone (0.4 g) was dissolved in 2 ml of concentrated sulfuric acid. On the next day the solution was diluted with water and the precipitated crystals were filtered off. The product - 0.24 g (59%) of crystals, m.p. 125-126° (from alcohol) - was identical with senecianilide.

b) 3-Bromo-3-methylbutyranilide (0.1 g) was added to a solution of 0.08 g of sodium hydroxide in methanol. On the next day water was added and the crystals precipitated were filtered off. The product - 0.6 g (87%) of crystals, m.p. 125-126° - was identical with (X).

Crotonanilide (XI)

a) 4-Methyl-1-phenyl-2-azetidinone (0.3 g) was dissolved in 1.5 ml of concentrated sulfuric acid. On the next day the solution was diluted with water and the crystals precipitated were filtered off. The crystals melted at 114-115° and were identical with crotonanilide.

b) 3-Bromobutyranilide (0.24 g) was added to a solution of 0.06 g of sodium hydroxide in methanol. After 15 minutes water was added and the crystals precipitated were filtered off. The product - 0.11 g (68%) of crystals, m.p. 114-115° - was identical with (XI).

N-Benzylcinnamamide (XII)

1-Benzyl-4-phenyl-2-azetidinone (1.4 g) was dissolved in 6 ml of concentrated sulfuric acid. On the next day the solution was diluted with water and the crystals precipitated were filtered off. The product, m.p. 103-104° (from alcohol), was identical with (XII).

SUMMARY

1. It was shown that, in presence of concentrated sulfuric acid, 4-phenyl-2-azetidinones are isomerized into 4-phenylhydrocarbostyrils.
2. Under the action of concentrated sulfuric acid, some N-substituted 2-azetidinones are converted into amides of α, β -unsaturated acids.
3. It was proved that the isomerization of 1-aryl-2-azetidinones into 4-phenylhydrocarbostyrils passes through the stage of amides of α, β -unsaturated acids.

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STERIC FACTOR IN ELECTROPHILIC SUBSTITUTION REACTIONS OF AROMATIC HYDROCARBONS

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In our studies of orientation in the chloro- and bromo-methylation of aromatic hydrocarbons (toluene, ethylbenzene, cumene, and tert-butylbenzene) [1] we encountered steric effects of substituents in the aromatic nucleus which influenced the proportions of o- and p-isomers formed. Thus, halomethylation of toluene gave 52% of o-isomers, halomethylation of ethylbenzene gave about 24% of o-isomers, cumene gave only about 13% of o-isomers, and in the case of tert-butylbenzene no o-isomer could be detected.

The marked reduction in content of o-isomers and corresponding increase in that of p-isomers as we pass from toluene, through ethylbenzene and cumene, to tert-butylbenzene must undoubtedly be attributed to the steric effects of the substituents: as these become more bulky, their screening effect on the adjacent o-positions increases and the halomethylation reaction is therefore directed into the p-position. Similar observations have been made previously for the nitration of this series of hydrocarbons [2] and also for some cases of halogenation and propylation [3]. However, these observations have generally been based on isolated experimental data from various papers by different authors in which the proportions of o-, m-, and p-isomers have been determined by different methods. Hence, not only are certain interesting data on the steric effects of substituents, e.g., for halogenation, absent but there are also contradictory data. For example, according to the literature, the nitration of cumene gives 86% of p- and 14% of o-isomer [4], whereas nitration of tert-butylbenzene gives 77% of p- and 23% of o-isomer [5]: on the basis of steric considerations it would be expected that for tert-butylbenzene the yield of o-isomer would be still lower than the yield given by cumene.

It therefore became urgent to make a systematic investigation of the steric effects of substituents in aromatic hydrocarbons on orientation in electrophilic substitution reactions. Work of this sort is of fundamental importance for the elucidation of the mechanisms and laws of these important reactions.

The present paper describes an investigation of the relative amounts of o- and p-isomers formed in the nitration, chlorination, bromination, and iodination of toluene, ethylbenzene, and cumene. The quantitative ortho-para ratio was established by the oxidation method, which we have previously used successfully [1] for halomethylation reactions. This method is based on the fact that chromium trioxide effects smooth oxidation to the corresponding substituted benzoic acids only in the case of the m- and p-isomers, the o-isomer being completely destroyed under these conditions. Hence, by submitting pure p-isomer and the investigated mixture of o- and p-isomers to oxidation with chromium trioxide under identical conditions, we may determine the quantitative proportions of these isomers in the mixture with fair accuracy. The amount of p-isomer is determined directly from the yield of p-substituted benzoic acid (in the case of the m-isomer - m-substituted benzoic acid), and the amount of o-isomer is calculated from the difference in yields of p-substituted benzoic acid obtained in the oxidation of pure p-isomer and of the investigated mixture of o- and p-isomers.

This method for the quantitative determination of o-, m-, and p-isomers was supplemented by oxidation of the investigated mixture with dilute nitric acid at high temperature ($\sim 200^\circ$) [6], by which not only m- and p-, but also o-isomers are oxidized smoothly with formation in high yield of the corresponding substituted benzoic acids, which may be separated directly. Such oxidation, however, did not give satisfactory results in the case of iodo compounds, evidently owing to the partial oxidation of iodine in the aromatic nucleus under these conditions. The small amounts of m-isomers formed in the nitration of the hydrocarbons were not determined. Our results on the relative extents of o- and p-substitution in the nitration, chlorination, bromination,

TABLE 1

Amounts of o- and p-Isomers Formed in the Nitration of Aromatic Hydrocarbons

Hydrocarbon	Amounts of isomers formed (%)	
	p-Isomer	o-Isomer
$C_6H_5CH_3$	32.5	67.5
$C_6H_5CH_2CH_3$	44.4	55.6
$C_6H_5CH(CH_3)_2$	60.5	39.5

TABLE 2

TABLE 2

Amounts of o- and p-Isomers Formed in the Chlorination of Aromatic Hydrocarbons

Hydrocarbon	Amounts of isomers formed (%)	
	p-Isomer	o-Isomer
$C_6H_5CH_3$	36	64
$C_6H_5CH_2CH_3$	50	50
$C_6H_5CH(CH_3)_2$	63.2	36.8

TABLE 3

Amounts of o- and p-Isomers Formed in the Bromination of Aromatic Hydrocarbons

Hydrocarbon	Amounts of isomers formed (%)	
	p-isomer	o-isomer
$C_6H_5CH_3$	58.5	41.5
$C_6H_5CH_2CH_3$	82	18
$C_6H_5CH(CH_3)_2$	89	11

TABLE 4

Amounts of o- and p-Isomers Formed in the Iodination of Aromatic Hydrocarbons

Hydrocarbon	Amounts of isomers formed (%)	
	p-isomer	o-isomer
$C_6H_5CH_3$	60	40
$C_6H_5CH_2CH_3$	95	5
$C_6H_5CH(CH_3)_2$	100	0

TABLE 5

Amounts of o- and p-Isomers Formed in the Chloromethylation of Aromatic Hydrocarbons

Hydrocarbon	Amounts of isomers formed (%)	
	p-isomer	o-isomer
$C_6H_5CH_3$	48.3	51.7
$C_6H_5CH_2CH_3$	77.3	22.7
$C_6H_5CH(CH_3)_2$	87.2	12.8

TABLE 6

Amounts of o- and p-Isomers Formed in the Bromomethylation of Aromatic Hydrocarbons

Hydrocarbon	Amounts of isomers formed (%)	
	p-isomer	o-isomer
$C_6H_5CH_3$	48.3	51.7
$C_6H_5CH_2CH_3$	75.7	24.3
$C_6H_5CH(CH_3)_2$	86.7	13.3

and iodination of toluene, ethylbenzene, and cumene are presented in the tables.

For comparison we give also the data we obtained previously [1] on the ortho-para ratio in the halomethylation of toluene, ethylbenzene, and cumene.

Comparison of our results with data in the literature indicates that the method we used previously for the determination of the ortho-para ratio for halomethylation can be extended successfully to cases of nitration and halogenation of aromatic hydrocarbons. Comparison of the relative amounts of isomers formed in the chlorination, bromination, and iodination of

TABLE 7

Relative Amount (%) of

Hydrocarbon	Chlorination	Bromination	Iodination
$C_6H_5CH_3$	64	41.5	40
$C_6H_5CH_2CH_3$	50	18	5
$C_6H_5CH(CH_3)_2$	36.8	11	0

toluene, ethylbenzene, and cumene shows that the relative amount of o-isomer (and therefore also of p-isomer) formed depends greatly on the identity of the halogenating agent.

TABLE 8

Relative Amounts of o- and p- Isomers in the Chlorination of Aromatic Compounds with Chlorine and with Ferric Chloride

Original compound	Proportions of o- and p-isomers (%)			
	Action of chlorine		Action of FeCl ₃	
	o-isomer	p-isomer	o-isomer	p-isomer
C ₆ H ₅ CH ₃	58	42	12	88
C ₆ H ₅ Cl	46	54	11	88
C ₆ H ₅ Br	42	51	13	87

It was later established that both in the case of nitric acid and in the case of nitration mixture the nitrating agent is the nitronium cation NO₂⁺. On the other hand it was found [9] that the chlorination of toluene and halobenzenes with elementary chlorine differs greatly from chlorination with ferric chloride (without chlorine) from the point of view of the relative amounts of isomers formed. In the second case the process results mainly in the formation of p-isomer and has a different mechanism from that operating in direct halogenation.

Now that we had a simple and rapid method for determining the relative amounts of o- and p-isomers formed in the nitration and halogenation of aromatic hydrocarbons, we undertook an investigation of the possibility of altering the composition of the mixture formed by changes in the methods of nitration and halogenation. Apart from nitration with nitration mixture, described above, we nitrated the hydrocarbons with concentrated nitric acid and with cupric nitrate in acetic anhydride [10]. It was shown that in both cases the mixture formed had the same composition as in nitration with nitration mixture. This result indicates that all these methods of nitration operate with the same nitrating agent (the nitronium cation). Bromination of toluene with dioxane dibromide gave a mixture of isomers having the same composition as in the case of bromination with bromine. This indicates that the brominating agent is the same in the two cases, i.e., bromination with dioxane dibromide is accompanied by dissociation of this compound with formation of bromine. This halogenation mechanism differs greatly from the above-mentioned mechanism of chlorination with ferric chloride, in which the chlorinating agent is ferric chloride itself (or its complexes), a circumstance that greatly influences the steric effect of substituents.

EXPERIMENTAL

Nitration of Aromatic Hydrocarbons with Nitration Mixture

a) Nitration mixture (63 ml of concentrated sulfuric acid and 50 ml of nitric acid, sp.gr. 1.42) was added over a period of 110 minutes to 46 g of toluene with stirring. The reaction temperature was not allowed to exceed 40°. When the whole of the nitration mixture had been added, the reaction mixture was poured into water, the precipitated oil was separated, the aqueous layer was extracted with ether, and the ether solution, after being combined with the oil, was washed with water and dried over calcium chloride. Fractionation gave 59 g (86%) of a mixture of mononitrotoluenes, b.p. 93–103° (10 mm). The residue (5.4 g), which solidified when allowed to stand, contained the products of further nitration. About 20% of crystalline p-isomer, m.p. 52–52.5°, was isolated from the mixture of mononitrotoluenes by cooling it to -15°.

b) By a similar procedure, from 53 g of ethylbenzene and the same amount of nitration mixture added over a period of 80 minutes at a temperature not exceeding 25°, 61 g (89%) of a mixture of mononitro

This regular reduction in the proportion of o-isomer formed with increase in the bulk of the halogen substituent is evidently also associated with increase in steric hindrance at the o-position. This behavior was first observed by Holleman [7], who constructed a series of groups arranged in order of increasing effective bulk, or, what amounts to the same, increasing hindrance to entry into the o-position: Cl, NO₂, Br, SO₃H.

The examination of the proportions in which isomers are formed is of importance for the elucidation of reaction mechanisms, for in reactions in which the attacking agent is the same the same proportions of isomers would be expected. It has been shown [8] that nitration of toluene with nitric acid and with acetyl nitrate gives mixtures of isomers of the same composition.

derivatives, b.p. 100–111° (10 mm), was obtained. The residue from the distillation amounted to 2.7 g; 4.8 g of unchanged ethylbenzene was recovered.

c) From 60 g of cumene and the same amount of nitration mixture added over a period of 100 minutes at a temperature not exceeding 30° we obtained 72.2 g (87.5%) of a mixture of mononitro derivatives, b.p. 110–120° (10 mm). The residue from the distillation amounted to 2.2 g.

Nitration of Aromatic Hydrocarbons with Concentrated Nitric Acid (sp. gr. 1.52)

In this case the hydrocarbon was added fairly rapidly to the nitric acid at a temperature not exceeding 30°. For nitration in this manner yields of mononitro derivatives were lower owing to formation of products of further nitration. When 21.4 g of toluene was added over a period of 10 minutes to 70 g of nitric acid at about 30°, 15.4 g of a mixture of mononitrotoluenes was obtained. Under the same conditions, 37 g of ethylbenzene and 105 g of nitric acid gave 24.6 g of a mixture of mononitro derivatives, and 42 g of cumene and 105 g of nitric acid gave 30 g of a mixture of mononitrocumenes.

Nitration of Aromatic Hydrocarbons with the aid of Cupric Nitrate in Acetic Anhydride

a) Acetic anhydride (150 ml) was added to finely ground cupric nitrate trihydrate (45 g). When this mixture had formed into an amorphous green mass, a solution 23 g of toluene in 150 ml of acetic anhydride was added in small portions. The reaction mixture was then poured onto ice, the precipitated oil was separated, the aqueous layer was extracted with ether, and the ether solution, after being combined with the oil, was washed with water and dried over calcium chloride. Fractionation gave 24.5 g (71.6%) of a mixture of mononitrotoluenes, b.p. 88–93° (8 mm); the residue amounted to 1.4 g.

b) Under similar conditions, 27 g of ethylbenzene gave 28.7 g (76%) of a mixture of mononitro derivatives, b.p. 103–114° (10 mm); the residue amounted to 1.5 g.

c) Under similar conditions, 30 g of cumene gave 30.2 g (73.3%) of a mixture of mononitrocumenes, b.p. 117–126° (12 mm); residue 0.8 g.

Oxidation of Mononitro Derivatives with Chromium Trioxide in Acetic Acid

a) A mixture of 2 g of p-nitrotoluene (m.p. 52–52.5°), 13 g of chromium trioxide, 30 ml of water, 30 ml of acetic acid, and 10 ml of concentrated sulfuric acid was refluxed until exothermic oxidation set in. When heat ceased to be evolved, the reaction mixture was boiled further for one hour. It was then cooled, and the precipitate was filtered off and dried. The product, amounting to 2.20 g (90%), was p-nitrobenzoic acid, m.p. 237.5–239°, undepressed by admixture of a known sample. When the experiment was repeated, 2.19 g of p-nitrobenzoic acid was obtained.

In the oxidation under strictly identical conditions of mixtures of isomeric mononitro derivatives, the following results were obtained.

b) From 2 g of the mixture of mononitrotoluenes obtained by nitration of toluene with nitration mixture, 0.71 g (29. %) of p-nitrobenzoic acid, m.p. 238–240°, was obtained. A repeat experiment yielded 0.71 g of p-nitrobenzoic acid.

c) From 2 g of the mixture of mononitrotoluenes remaining after the freezing out of 18% of crystalline p-isomer, 0.42 g (17.3%) of p-nitrobenzoic acid was obtained. A repeat experiment yielded 0.41 g of p-nitrobenzoic acid.

d) From 2 g of the mixture of mononitrotoluenes obtained by nitration of toluene with concentrated nitric acid, 0.72 g of p-nitrobenzoic acid, m.p. 238–240°, was obtained. A repeat experiment yielded 0.70 g of p-nitrobenzoic acid.

e) From 2 g of the mixture of mononitrotoluenes obtained by nitration of toluene with cupric nitrate in acetic anhydride, 0.66 g of p-nitrobenzoic acid, m.p. 237–239°, was obtained. In admixture with the above-described samples there was no depression of melting point.

f) From 2 g of the mixture of ethylnitrobenzenes obtained by nitration of ethylbenzene with nitration mixture, 0.88 g (40%) of p-nitrobenzoic acid, m.p. 237–239°, was obtained. A repeat experiment yielded 0.87 g of p-nitrobenzoic acid.

g) From 2 g of the mixture of ethylnitrobenzenes obtained by nitration of ethylbenzene with concentrated nitric acid, 0.81 g of p-nitrobenzoic acid, m.p. 238–239°, was obtained.

h) From 2 g of the mixture of ethylnitrobenzenes obtained by nitration of ethylbenzene with cupric nitrate in acetic anhydride, 0.82 g of p-nitrobenzoic acid, m.p. 237–239°, was obtained. A repeat experiment yielded 0.82 g of p-nitrobenzoic acid.

i) From 2 g of the mixture of mononitrocumenes obtained by nitration of cumene with nitration mixture, 1.09 g (54%) of p-nitrobenzoic acid, m.p. 237–239°, was obtained. A repeat experiment yielded 1.08 g of p-nitrobenzoic acid.

j) From 2 g of the mixture of mononitrocumenes obtained by nitration of cumene with concentrated nitric acid, 1.10 g of p-nitrobenzoic acid, m.p. 238–239°, was obtained.

k) From 2 g of the mixture of mononitrocumenes obtained by nitration of cumene with cupric nitrate in acetic anhydride, 1.10 g of p-nitrobenzoic acid, m.p. 237–239°, was obtained. A repeat experiment yielded 1.07 g of p-nitrobenzoic acid.

The identity of the results for the oxidation of mononitro derivatives obtained by various methods of nitration will be seen from Table 9.

TABLE 9

Amounts (g) of p-Nitrobenzoic Acid Obtained by Oxidation of 2 g of a Mixture of Mononitro Derivatives of Aromatic Hydrocarbons

Nitrating agent	$C_6H_5CH_3$	$C_6H_5CH_2CH_3$	$C_6H_5CH(CH_3)_2$
Nitration mixture	0.71	0.88	1.09
Concentrated nitric acid	0.72	0.81	1.10
Cupric nitrate in acetic anhydride	0.66	0.82	1.10

Oxidation of Mixtures of Mononitro Derivatives with Dilute Nitric Acid at 200°

a) A 200-ml rotating autoclave was charged with 30 ml of 20% nitric acid and 5 g of a mixture of mononitrotoluenes. The contents were agitated at 200° for 90 minutes. They were then cooled, and p-nitrobenzoic acid [2.42 g, m.p. 237–238° (from water)] was filtered off; there was no depression of melting point in a mixture test. After being evaporated down to low bulk, the mother liquor gave 2.07 g of o-nitrobenzoic acid, which was purified through its ammonium salt and recrystallized from benzene (m.p. 142–144°; the literature gives 144–145°). The total yield of acids was 75%. The low yield of o-nitrobenzoic acid, here and in other cases of oxidation of o-isomers with dilute nitric

acid, is to be attributed to less quantitative reaction, as compared with the p-isomers, and to difficulty in isolation of o-substituted benzoic acids owing to their higher solubility.

In the oxidation of mixtures of other mononitro derivatives under similar conditions, the following results were obtained.

b) From 5 g of a mixture of ethylnitrobenzenes and 40 ml of 20% nitric acid, 2.53 g of p-nitrobenzoic acid, m.p. 237–238°, and 1.92 g of o-nitrobenzoic acid, m.p. 142–144°, were obtained. Total yield of acids 80.4%.

c) From 5 g of a mixture of mononitrocumenes and 50 ml of 20% nitric acid, 2.98 g of p-nitrobenzoic acid, m.p. 237–238°, and 0.80 g of o-nitrobenzoic acid, m.p. 142–143°, were obtained. Total yield of acids 74.7%.

Chlorination of Aromatic Hydrocarbons

a) Chlorine was passed for 30 minutes (increase in weight 25 g) into a stirred mixture of 92 g of toluene and 0.5 g of ferric chloride at a temperature not exceeding 20°. The reaction mixture was washed first with water, then sodium bicarbonate solution, and finally with water again, and was then dried over calcium chloride. After distillation of excess of toluene and a small head fraction (8.3 g), we obtained 55.3 g (78.5%) of a mixture of monochlorotoluenes, b.p. 157–160°; the residue from the distillation amounted to 9.6 g.

b) Reaction under similar conditions between 106 g of ethylbenzene, 0.5 g of ferric chloride, and 23 g

(according to increase in weight) of chlorine for 75 minutes gave 58.8 g (81%) of a mixture of monochloroethylbenzenes, b.p. 58–63° (13 mm). The head fraction amounted to 2.05 g, and the residue to 8.9 g.

c) From 120 g of cumene, 0.5 g of ferric chloride, and 24.7 g of chlorine (according to increase in weight), reacting for one hour, we obtained 56.6 g of a mixture of mononitrocumenes, b.p. 69–76° (14 mm). The head fraction amounted to 6.3 g, and the residue to 14.2 g.

Bromination of Aromatic Hydrocarbons

a) A mixture of 53 ml of toluene and 20 ml of bromine was heated at 45° for four hours. The reaction mixture was washed with water, with 10% NaOH solution, and again with water, and was then dried over calcium chloride. After distillation of a little unchanged toluene (4.7 g), we obtained 44.6 g (65.2%) of a mixture of monobromotoluenes, b.p. 76–80° (18 mm). The residue from the distillation amounted to 14 g. By a freezing treatment, about 30% of the crystalline *p*-isomer, m.p. 26–28°, was isolated from the mixture of monobromotoluenes.

b) Reaction of 53 ml of ethylbenzene with 20 ml of bromine under similar conditions gave 38.7 g (52.3%) of a mixture of bromoethylbenzenes, b.p. 86–90° (18 mm). We obtained also 11.2 g of unchanged ethylbenzene and 22 g of residue.

c) The bromination of cumene under similar conditions proceeds in a very complicated manner, and the yield of monobromocumenes is only 7–10%. At the same time a large amount of high-boiling products is obtained in the bromination of cumene in presence of iodine.

A mixture of 20 g of cumene and 2.5 g of iodine was cooled with a mixture of ice and salt, and 27 g of bromine was added dropwise over 5.5 hours. The reaction mixture was washed with water, with 10% NaOH solution, and again with waters and was then dried over calcium chloride. Fractionation gave 21.5 g (65%) of a mixture of monobromocumenes, b.p. 97–99° (19 mm). The head fraction amounted to 3.3 g, and the residue to 2.7 g.

Bromination of Toluene with Dioxane Dibromide

A mixture of 23 g of toluene and 62 g of dioxane dibromide was heated at 50–60° for the very short time necessary for the intensity of the color of the solution to fall sharply. The hydrocarbon layer was then washed with sodium thiosulfate solution, with sodium bicarbonate solution, and with water, and was dried over calcium chloride. A little unchanged toluene (3.0 g) was distilled off, and further distillation gave 26.3 g (70.7%) of monobromotoluenes, b.p. 57–60° (8 mm); residue from distillation 5.3 g.

Iodination of Aromatic Hydrocarbons [11]

a) Nitric acid (2.6 g, sp. gr. 1.39) was added over a period of 40 minutes to a stirred mixture of 17 ml of toluene, 12.7 g of iodine, 40 ml of acetic acid, and 11 ml of sulfuric acid at 45°. The reaction mixture was then stirred further for 10 minutes at 45°. The oil formed was washed with 10% NaOH solution and then water. The wash waters were shaken with ether, and the ethereal solution was dried over calcium chloride. In the distillation a small head fraction (1.4 g) was followed by 19.15 g (55.5%) of a mixture of monoiodotoluenes, b.p. 92–93° (18 mm). From this by a freezing treatment, about 30% of the crystalline *p*-isomer, m.p. 32–33°, was isolated.

b) Under similar conditions, 17 ml of ethylbenzene gave 21.3 g (66.3%) of a mixture of ethyliodobenzenes, b.p. 104–106° (17 mm).

c) From 17 ml of cumene we obtained 8.7 g (29.1%) of *p*-iodocumene, b.p. 112–115° (17 mm); 8.3 g of cumene was recovered unchanged.

Oxidation of Monochloro Derivatives with Chromium Trioxide in Acetic Acid

a) A mixture of 2 g of *p*-chlorotoluene, specially prepared from *p*-toluidine, 12 g of chromium trioxide, 30 ml of water, 30 ml of acetic acid, and 10 ml of concentrated sulfuric acid was refluxed until exothermic oxidation set in. When heat evolution ceased, the reaction mixture was boiled further for one hour. After cooling, filtering, and drying, we obtained 1.70 g (69%) of *p*-chlorobenzoic acid, m.p. 238–239°, undepressed by admixture of a known sample. A repeat experiment yielded 1.74 g of *p*-chlorobenzoic acid.

Oxidation under strictly identical conditions gave the following results:

b) From 2.0 g of the mixture of monochlorotoluenes obtained in the chlorination of toluene we prepared 0.62 g (25.1%) of *p*-chlorobenzoic acid, m.p. 237–239°. A repeat experiment yielded 0.61 g of *p*-chlorobenzoic acid.

c) From 2.0 g of the mixture of monochloroethylbenzenes we obtained 0.77 g (34.6%) of *p*-chlorobenzoic acid, m.p. 238–240°. A repeat experiment gave 0.76 g of *p*-chlorobenzoic acid.

d) From 2.0 g of monochlorocumenes we obtained 0.89 g (44%) of *p*-chlorobenzoic acid, m.p. 237–239°. A repeat experiment gave 0.87 g of *p*-chlorobenzoic acid.

Oxidation of Mixtures of Monochloro Derivatives with Nitric Acid at 200°

a) A 200-ml rotating autoclave was charged with 60 ml of 20% nitric acid and 5.0 g of the mixture of monochlorotoluenes. The contents were agitated at 200° for 90 minutes. From the cooled reaction mixture, 4.0 g (64.7%) of a mixture of *o*- and *p*-chlorobenzoic acids was filtered. The isomers were separated through their calcium salts, as follows. The mixture (2 g) was dissolved in aqueous ammonia, and the solution was filtered and boiled to remove excess of ammonia (judged by smell). A solution of pure calcium chloride was added to the solution of ammonium salts, and the less water-soluble calcium *p*-chlorobenzoate separated and was converted into the acid by treatment with dilute hydrochloric acid. In this way we isolated 1.1 g of pure *p*-chlorobenzoic acid, m.p. 238–240°, undepressed by admixture of a sample of this acid obtained by chromium trioxide oxidation. By evaporation of the mother liquor (calcium salts) to low bulk we obtained calcium *o*-chlorobenzoate, from which, after careful washing with alcohol to remove residual salt of the *p*-acid, we isolated *o*-chlorobenzoic acid, m.p. 137–138° (from water), by acidification with dilute hydrochloric acid.

b) By oxidation under similar conditions, from 5.0 g of the mixture of monochloroethylbenzenes and 70 ml of 20% nitric acid we obtained 4.26 g (36.6%) of a mixture of chlorobenzoic acids.

c) From 5.0 g of the mixture of monochlorocumenes and 75 ml of 20% nitric acid we obtained 3.5 g (70%) of a mixture of chlorobenzoic acids. In this and the previous experiment we isolated *p*-chlorobenzoic acid, m.p. 238–240°, and *o*-chlorobenzoic acid, m.p. 137–138°, through their calcium salts.

Oxidation of Monobromo Derivatives with Chromium Trioxide in Acetic Acid

a) A mixture of 2.0 g of *p*-bromotoluene (m.p. 26–28°), 9 g of chromium trioxide, 30 ml of water, 30 ml of acetic acid, and 9 ml of concentrated sulfuric acid was refluxed until exothermic oxidation set in. When heat ceased to be evolved, the reaction mixture was boiled further for one hour. After cooling, filtering, and drying, we obtained 1.63 g (70.5%) of *p*-bromobenzoic acid, m.p. 252–254°. A repeat experiment gave 1.57 g of *p*-bromobenzoic acid.

Oxidation under strictly identical conditions gave the following results.

b) From 2.0 g of the mixture of monobromotoluenes obtained in the bromination of toluene with bromine we prepared 0.95 g (40.4%) of *p*-bromobenzoic acid, m.p. 252–254°. A repeat experiment gave 0.96 g of *p*-bromobenzoic acid.

c) From 2.0 g of the mixture of monobromotoluenes remaining after separation of 30% of crystalline *p*-isomer, we obtained 0.69 g (29.3%) of *p*-bromobenzoic acid, m.p. 252–254°.

d) From 2.0 g of the mixture of monobromotoluenes formed in the bromination of toluene with dioxane dibromide we obtained 1.0 g (42%) of *p*-bromobenzoic acid, m.p. 252–254°. A repeat experiment gave 0.90 g of *p*-bromobenzoic acid.

e) From 2.0 g of the mixture of monobromoethylbenzenes formed in the bromination of ethylbenzene with bromine, we obtained 1.25 g (57.6%) of *p*-bromobenzoic acid, m.p. 252–254°. A repeat experiment gave 1.25 g of *p*-bromobenzoic acid.

f) From 2.0 g of the mixture of monobromocumenes formed in the bromination of cumene with bromine we obtained 1.00 g (50%) of *p*-bromobenzoic acid, m.p. 252–254°.

Oxidation of Mixtures of Monobromo Derivatives with Dilute Nitric Acid at 200°

a) A 200-ml rotating autoclave was charged with 50 ml of 20% nitric acid and 5.0 g of a mixture of monobromotoluenes. The contents were agitated at 200° for 90 minutes. From the cooled reaction mixture, 2.73 g of bromobenzoic acids was filtered. Evaporation of the mother liquor gave a further 1.09 g of

bromobenzoic acids. The smaller difference in solubility between the *o*- and *p*-isomers, as compared, for example, with the nitrobenzoic acids, results in the presence of much *o*-isomer in the precipitated bromobenzoic acid and in considerable contamination with *p*-isomer of the product isolated from the mother liquor. The total yield of bromobenzoic acids was 4.42 g (75.3%). By recrystallization of the 2.73 g of precipitated acid we obtained 1.63 g of *p*-bromobenzoic acid, m.p. 248–250° (from dilute acetic acid), undepressed by admixture of the above-described samples obtained by chromium trioxide oxidation. The isolation of pure *o*-bromobenzoic acid from the 1.69 g of bromobenzoic acids obtained by evaporation of the mother liquor is associated with long purification processes consisting in conversion into a salt and repeated recrystallization. *o*-Bromobenzoic acid obtained by purification through the silver salt, which was recrystallized repeatedly from water, had m.p. 143–145° (the literature gives 147–148°).

b) By oxidation under similar conditions, from 5.0 g of the mixture of monobromoethylbenzenes and 60 ml of 20% nitric acid we obtained 3.72 g (68.5%) of a mixture of *o*- and *p*-bromobenzoic acids (2.31 g was filtered off, and 1.41 g was obtained by evaporation of the mother liquor).

c) From 5.0 g of monobromocumenes and 70 ml of 20% nitric acid we obtained 3.57 g (70.6%) of a mixture of *o*- and *p*-bromobenzoic acids (2.82 g by filtration and 0.75 g from mother liquor). In this and the previous experiment we isolated pure *o*- and *p*-bromobenzoic acids by the method described above.

Oxidation of Monoiodo Derivatives with Chromium Trioxide in Acetic Acid

a) A mixture of 2.0 g of *p*-iodotoluene (m.p. 32–33°), 8 g of chromium trioxide, 30 ml of water, 30 ml of acetic acid, and 8 ml of concentrated sulfuric acid was refluxed until exothermic oxidation set in. When heat ceased to be evolved, the reaction mixture was boiled further for one hour. After cooling, filtration, and drying, we obtained 1.14 g (50%) of *p*-iodobenzoic acid, m.p. 270–272°.

b) By oxidation under the above-described conditions, from 2.0 g of the mixture of monoiodotoluenes formed in the iodination of toluene we obtained 0.71 g (31%) of *p*-iodobenzoic acid, m.p. 269–271°. A repeat experiment gave 0.69 g of *p*-iodobenzoic acid.

c) In the oxidation of 2.0 g of the mixture of monoiodotoluenes remaining after 30% of crystalline *p*-isomer had been frozen out, we obtained 0.47 g (21%) of *p*-iodobenzoic acid, m.p. 269–271°. A repeat experiment gave 0.42 of *p*-iodobenzoic acid.

d) In the oxidation of 2.0 g of the mixture of ethyliodobenzenes we obtained 1.02 g (47.8%) of *p*-iodobenzoic acid, m.p. 270–272°. A repeat experiment gave 1 g of *p*-iodobenzoic acid.

e) In the oxidation of 2.0 g of the mixture of monoiodocumenes we obtained 1.01 g (50.2%) of *p*-iodobenzoic acid, m.p. 270–272°. A repeat experiment gave 1 g of *p*-iodobenzoic acid.

SUMMARY

In supplementation of previous work on halomethylation reactions, the nitration, chlorination, bromination, and iodination of toluene, ethylbenzene, and cumene were investigated. By the method of oxidizing the derivatives formed, the relative amounts of *o*- and *p*-isomers were determined quantitatively, and the results reveal the steric effects of substituents in the aromatic nucleus on orientation in all of the above-mentioned electrophilic substitution reactions.

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OXIDATION-REDUCTION SYSTEMS FOR THE INITIATION OF FREE-RADICAL PROCESSES

COMMUNICATION 5. OXIDATION-REDUCTION SYSTEMS FOR THE VULCANIZATION OF RUBBERS IN HYDROCARBON SOLUTIONS

E. I. Tinyakova, B. A. Dolgoplosk, and V. N. Reikh

It is well known that many polymerization initiators – organic peroxides and hydroperoxides, diazoamino compounds, etc. act at their decomposition temperatures as powerful vulcanizing cross-linking agents for rubbers [1]. The vulcanizing effect is due to reaction of free radicals with the polymer chain by addition to C=C bonds or removal of an H atom, which is followed by the development of a chain process leading to the formation of a three-dimensional structure. In this case the chain is very short and must correspond in length to the chain in the polymerization of olefins used as models of the structure of the polymer. In the reaction of free-radicals with 1-heptene or isobutene, the chain is made up of 2-4 links [2]. For α -olefins this reaction has not yet been studied. Apart from this, there appear to be no essential qualitative features distinguishing vulcanization of this type from polymerization.

It is generally known that oxidation-reduction systems have now acquired great importance for the initiation of polymerization in aqueous emulsions and have made it possible to carry out the process at much lower temperatures than those required for the thermal decomposition of initiators. In a previous investigation we showed that it is possible to use certain reversible systems for the initiation of polymerization in a homogeneous hydrocarbon medium [3]. As the initiation stage (formation of the initial active centers) usually determines the over-all rate of chain processes, we considered that it was possible in principle to use oxidation-reduction systems for the initiation of other free-radical processes in hydrocarbon media at low temperatures, in particular processes of vulcanization (cross linking) and degradation of polymers and oxidation processes. The present communication is devoted to a study of various oxidation-reduction systems in hydrocarbon media and an examination of their vulcanizing effect on unsaturated polymers.

EXPERIMENTAL

a) System consisting of Benzoyl Peroxide, Diethyl Dihydroxymaleate, and Ferric Naphthenate. Systems consisting of cumene hydroperoxide, dienols (ascorbic or dihydroxymaleic acid), and traces of iron salts are among the most effective for the initiation of polymerization in emulsions [4]. When dihydroxymaleic acid is replaced by its diethyl ester and the hydrocarbon-soluble ferric naphthenate is used, the system may initiate polymerization in a hydrocarbon medium at 50° [3]. In absence of monomer, the same system can bring about the vulcanization of rubber. When benzoyl peroxide and an equimolecular amount of diethyl dihydroxymaleate or benzoyl peroxide together with ferric naphthenate is added to a polybutadiene solution, the viscosity of the solution remains unchanged (Curves 1 and 2, Figure 1). There is an effect only when all three components are present simultaneously: the viscosity of the solution then rises rapidly (Curve 3, Figure 1). When the solution is allowed to stand undisturbed, within two hours it is converted completely and irreversibly into a gel.

There is an initial "induction" period during which the viscosity of the solution remains unchanged or even falls somewhat. This induction period arises from inadequate removal of oxygen from the system. When there is sufficient access to air, degradation processes begin to predominate and the viscosity of the solution falls

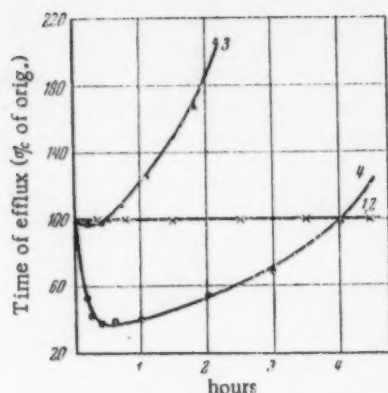


Fig. 1. Change in viscosity of a solution of SKB rubber (polybutadiene) at 20° in presence of benzoyl peroxide (BP), diethyl dihydroxymaleate (DDM), and ferric naphthenate (FN): 1) BP + DDM; 2) BP + FN; 3) BP + DDM + FN; 4) = 3) but with limited access to air.

continuously. When a limited amount of air is introduced (12–13 ml of air per 10 ml of rubber solution), the induction period is lengthened, but when oxygen has been used up the vulcanization process proceeds at its usual rate (Curve 4, Fig. 1). The initial sections of Curves 3 and 4 represent the resultant of the superposition of two processes – vulcanization under the action of free radicals and oxidative degradation of the chain occurring under the same conditions with participation of oxygen. The inhibiting role of oxygen in the vulcanization process of the polymer is completely analogous with its inhibiting effect on polymerization initiated by oxidation–reduction systems of the type under discussion. We are dealing with two competing chain reactions, vulcanization and oxidation, which proceed through a free-radical stage. The predominance of oxidative processes over vulcanization in presence of oxygen is due to the low activity of the monomer units of the chain in polymerization reactions. It should be noted that the investigated butadiene rubber has a large number of ethylenic bonds in the chain (about 70% of the theoretical number), which no doubt favors vulcanization and is less favorable for oxidative degradation processes.

b) System consisting of Benzoyl Peroxide, Benzoin, and Ferric Naphthenate. This system was first used by Kern for initiation of polymerization in a homogeneous medium [5]. Owing to the lower reducing power of benzoin as compared with dihydroxymaleic ester, the decomposition of benzoyl peroxide in this system at 20° is considerably slower. The effect of this system on rubber solutions (Figure 2) is in full accord with the kinetics of the interaction of the components. In presence of benzoyl peroxide and benzoin or benzoyl peroxide and ferric naphthenate at 20°, the viscosity of the solution does not change. When all three components are present simultaneously, decomposition of benzoyl peroxide sets in under the influence of the ferrous iron formed and this results in vulcanization of the rubber. When the solution is allowed to stand undisturbed at 20°, within 16–18 hours the solution is converted completely into a gel. In this case there is again an induction period attributable to the same causes as before. In presence of a little air (12–13 ml of air per 10 ml of rubber solution), the

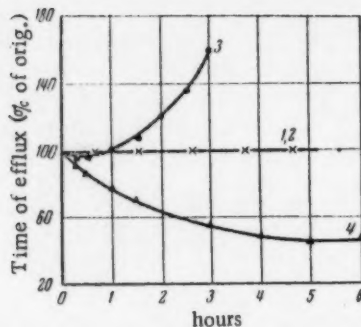


Fig. 2. Change in viscosity of a solution of SKB rubber at 20° in presence of benzoyl peroxide, benzoin, and ferric naphthenate; 1) BP + benzoin; 2) BP + FN; 3) BP + benzoin + FN; 4) = 3) but in presence of a limited amount of air.

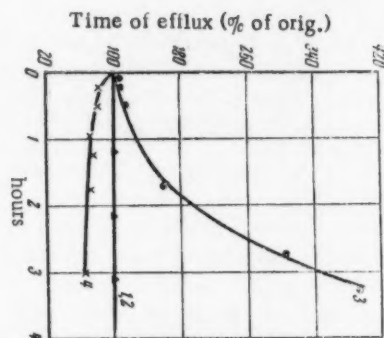


Fig. 3. Change in viscosity of a solution of SKB rubber at 20° in presence of benzoyl peroxide, triethylenetetramine (TETA) and ferric naphthenate: 1) BP + TETA; 2) BP + FN; 3) BP + TETA + FN; 4) = 3) but in presence of air.

induction period is lengthened and there is an intensification of the degradative processes in the initial stage (Fig. 2, Curve 4).

As would be expected, the rate of vulcanization in presence of benzoin is substantially lower than in presence of dihydroxymaleic ester. The longer induction period in the system under consideration is in accord with its lower activity, since, for a given oxygen content, the induction period varies inversely as the concentration of active centers. Hence, in absence of oxygen oxidation-reduction systems initiate the vulcanization process, and in presence of oxygen they initiate the oxidative degradation of polymers. This conclusion can be illustrated by other examples.

c) System consisting of Benzoyl Peroxide, Polyethylenepolyamine, and Ferric Naphthenate. Figure 3 gives kinetic curves for the change in viscosity of a solution of polybutadiene having a lower content (about 50%) of ethylenic bonds in presence of a system containing benzoyl peroxide, triethylenetetramine, and ferric naphthenate at 20°. As is well-known, such a system is highly effective for the initiation of polymerization in emulsions [6]. Unlike the reducing substances used in the systems discussed above, polyethylenepolyamines do not reduce Fe^{3+} to Fe^{2+} directly. The decomposition of the peroxide appears to be brought about by a complex formed by the polyethylenepolyamine with ferric salts. As in the other cases initiation of reaction occurred only when all three components of the system were present. In this case a rapid increase in the viscosity of the solution was observed. Introduction of small amounts of air resulted in the development of degradative processes (Curve 4, Fig. 3).

d) Systems containing Thiols. In emulsion and homogeneous polymerization, aliphatic thiols are often used to control the length of the polymer chain owing to their high tendency to take part in chain-transfer reactions [7]. In aqueous emulsions they cause increase in the rate of decomposition of the peroxide and therefore in the rate of polymerization. The action of the system appears to depend on the reaction:

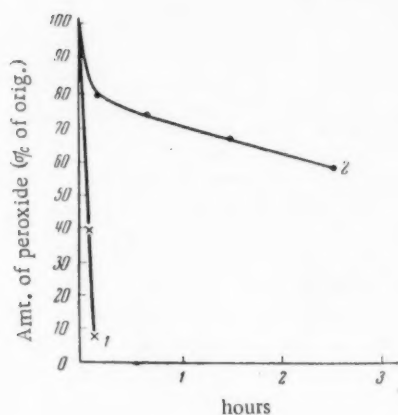


Fig. 4. Kinetics of the reaction of captax* with benzoyl peroxide (1) and cumene hydroperoxide (2) in solution at 20°.

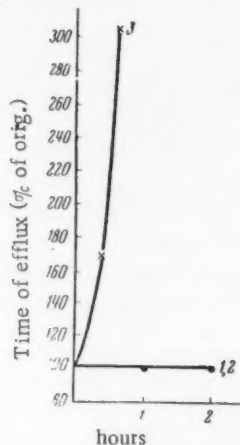
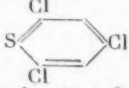


Fig. 5. Change in viscosity in a solution of SKB rubber in presence of cumene hydroperoxide (CH) and captax at 20°: 1) CH; 2) CH + captax; 3) = 2) in presence of air.

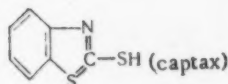
Energetically favorable conditions for reaction are the formation of oxidation products (water) and the production of more stable radicals. Thus, in the case of trichlorobenzenethiol, rupture of the S-H bond results

in the formation of the very stable radical $\text{S} \cdot$ . As we have shown, the oxidation of trichlorobenzenethiol proceeds very vigorously even under the influence of SO_2 , and it is accompanied at 0° by the vulcanization of rubbers [8]. Though the mechanism of this reaction is still rather obscure, there can be no

* Captax = mercaptobenzothiazide — Publisher's note.

doubt that the process proceeds under the influence of intermediate active reaction products and that this is a special case of the oxidation-reduction initiation of free-radical processes by systems not containing peroxides. The part played by intermediate reaction products is illustrated by the fact that in the course of reaction both reactants add extremely readily to an unsaturated polymer chain [8].

Study of the kinetics of the interaction of benzoyl peroxide and of cumene hydroperoxide with captax (mercaptobenzothiazole) in ethylbenzene solution showed that reaction is very rapid even at room temperature (Figure 4).



The oxidation of captax with cumene hydroperoxide also proceeds at 20°, but at a lower rate. Reaction between the hydroperoxide and captax can be used for the initiation of the vulcanization of rubber at 20° (Figure 5). Introduction of captax into a solution containing cumene hydroperoxide resulted in a sharp rise in the viscosity of the solution (Curve 2, Fig. 5). Within three hours the rubber solution had turned into a gel. The introduction of small amounts of air again resulted in suppression of the vulcanization process.

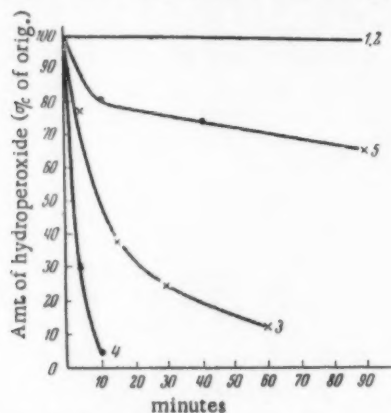


Fig. 6. Kinetics of interaction between cumene hydroperoxide, diphenylguanidine (DPG), and altax* or captax at 20° in solution: 1) CH + altax; 2) CH + DPG; 3) CH + DPG + altax; 4) CH + DPG + captax; 5) CH + captax.

In rubber technology extensive use is made of various combinations of accelerators in vulcanization and plasticization processes. In particular, a highly effective combination is that of diphenylguanidine and altax (2,2'-dithiobisbenzothiazole), and also that of diphenylguanidine and captax. We showed that, when both substances are present simultaneously, they react with the hydroperoxide much more effectively than does each separately (Figure 6). In an equimolecular mixture of hydroperoxide, altax, and diphenylguanidine at 20°, only about 12% of the original amount of hydroperoxide remains after one hour. Under these conditions, neither diphenylguanidine alone nor altax alone will react with the hydroperoxide.

A system containing cumene hydroperoxide, diphenylguanidine, and altax is very effective in the vulcanization of rubber: the viscosity of the solution rises, and within 1.5–2 hours the whole solution is converted into a gel (Figure 7). In presence of air there is a continuous fall in viscosity.

A combination of diphenylguanidine and captax is still more active. With equimolecular amounts of reactants at 20° the hydroperoxide is almost completely destroyed in ten minutes. Reaction between the

* Altax = 2,2'-dithiobisbenzothiazole – Publisher's note.

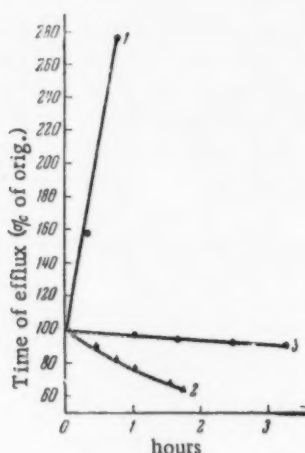
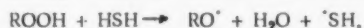


Fig. 7. Change in viscosity of a solution of SKB rubber in presence of cumene hydroperoxide, diphenylguanidine, and altax at 20°: 1) CH + DPG + altax; 2) 1) in presence of air; 3) CH + DPG in presence of air.

hydroperoxide and captax in absence of diphenylguanidine is much slower (compare Curves 4 and 5, Figure 6). The acceleration of reaction is probably due to the formation of complexes between altax or captax and diphenylguanidine. It may be noted that the reaction of altax with a peroxide is accelerated also by other amines, in particular N-phenyl-2-naphthylamine. In this last case the process is fairly rapid at 50°.

e) System consisting of a Peroxide and SO₂ or H₂S. Reaction of the hydroperoxide with SO₂ in hydrocarbon solution proceeds very rapidly and results in rapid gelling of a rubber solution. For example, when SO₂ was passed through a rubber solution containing cumene hydroperoxide (about 1%), within one minute there was complete gelation and conversion of the rubber into an insoluble form. In absence of the peroxide this process did not occur. In rubber solutions containing N-phenyl-2-naphthylamine, vulcanization is still more rapid: the whole solution is converted into a gel within 5-10 seconds from the introduction of SO₂. Very rapid vulcanization of rubber in solution is observed also when the peroxide reacts with sodium hydrosulfite (dithionite). In these experiments, the rubber solution containing cumene hydroperoxide or benzoyl peroxide was shaken with aqueous sodium hydrosulfite. Reaction at the interface of the two liquid phases resulted in gel formation in 1-2 minutes.

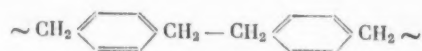
A similar effect is given by an oxidation-reduction system consisting of peroxides and hydrogen sulfide. The reaction probably passes through the stage of the formation of two radicals, e.g., as follows:



Hence, almost all reactions leading to increased rate of decomposition of peroxides and hydroperoxides in hydrocarbon media are accompanied by the development of free-radical chain processes that bring about the cross linking and degradation of polymers.

It is often recommended that termination of radical processes be brought about by the introduction of reducing agents capable of rapidly destroying peroxides or hydroperoxides present in the system. The results of the present work indicate the danger of such methods in the case of polymers. Under certain conditions, all the systems described are suitable for the process of the mass vulcanization of rubber. For most of the systems examined we have established the possibility in principle of bringing about such processes.

Cross linking and degradation are the most important chemical processes associated with the aging of polymers. It would appear that in the great majority of cases both processes are initiated from outside and do not arise from the purely thermal decomposition of the polymers at C—C and C—H bonds. Evidence in favor of such views is to be found in the exceptionally high thermal stability of poly(methylenephenyl) [9], in spite of the presence of a weak C—C bond.



The investigation shows that free-radical processes can be initiated by oxidation-reduction reactions proceeding at comparatively low temperatures with the participation of various substances present in polymers.

Procedure Followed in Study of the Action of Systems on Rubber Solutions

The effects of the systems were estimated from measurements of the viscosity of the solution. The experiments were carried out in special ampoule-viscometers (Figure 8). The volume of the bulb A was 2.5-3 ml, the diameter of the capillary was 2 mm, and its length was 50 mm.

The rubber solution was prepared in a measuring ampoule. Finely cut rubber was weighed into this ampoule, air was removed by means of an oil pump, and the apparatus was filled with oxygen-free nitrogen. The operation was repeated three times. Ethylbenzene was then introduced into the ampoule in a counter current of nitrogen. The viscometers containing a weighed amount of benzoyl peroxide were twice evacuated by means of an oil pump and filled with nitrogen, and in a counter current of nitrogen the rubber solution—containing, when necessary, ferric naphthenate was introduced from the measuring ampoule. The time of efflux of the volume of solution between the marks was determined. When the initial time of efflux had been determined in the viscometers, a weighed amount of reducing agent was introduced in a counter current of

nitrogen, and times of efflux were then determined at definite intervals of time. The viscosity measurements were made in a thermostat. The vulcanization effects of systems containing peroxides and H_2S or SO_2 were estimated only from the time required for gel formation when H_2S or SO_2 was passed through the rubber solution containing the peroxide.

The rubber concentration of the solution was 4.5% (mean time of efflux 2-5 minutes). The concentrations of benzoyl peroxide and of cumene hydroperoxide in the solutions were 0.34% and 0.22%, respectively. The amount of reducing agent added was 100 moles % on the amount of peroxide, and the amount of ferric naphthenate was 20 moles % on the peroxide.

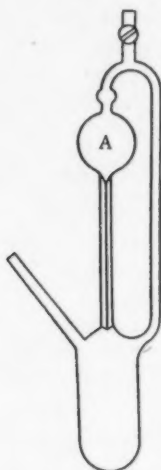


Fig. 8. Viscometer.

SUMMARY

1. It was established that oxidation-reduction systems consisting of peroxides or hydroperoxides and various reducing agents in hydrocarbon media are able to initiate the free-radical chain process of cross linking (vulcanization) of polymers at low temperatures.

2. Presence of oxygen results in the suppression of cross linking and the occurrence of oxidative degradation of the polymer.

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ACTION OF AMMONIA ON CYCLOHEPTANONE IN PRESENCE OF A NICKEL CATALYST

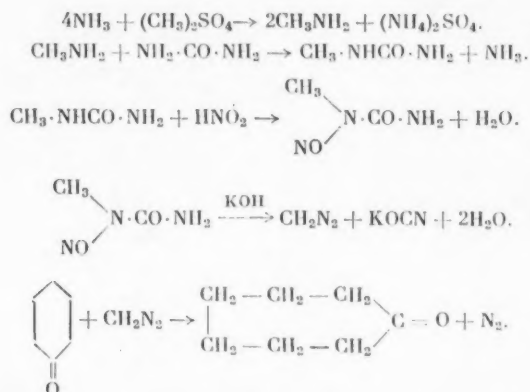
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We have shown in previous investigations [1] that the alicyclic ketones cyclopentanone and cyclohexanone readily undergo reductive amination. In continuation of our investigations on the catalytic synthesis of alicyclic amines, we studied the reaction of cycloheptanone with ammonia and hydrogen. In this reaction we might expect the formation of cycloheptylamine. This amine was first prepared by Markovnikov [2] by the reduction of cycloheptanone oxime and then by Willstätter [3] from cycloheptanecarboxamide. The properties of cycloheptylamine have not been adequately investigated. It might be expected also that at high temperature in presence of a catalyst conversion of the seven-membered ring into a smaller ring might occur.

The object of the present investigation was to determine which of these two possible directions the catalytic amination of cycloheptanone does in fact take. As catalyst we used reduced nickel on active alumina. It was shown by experiments with cyclopentanone that the catalyst had good amination properties and did not induce side reactions.

EXPERIMENTAL

Cycloheptanone was synthesized as follows:



Ethereal diazomethane was prepared by Eistert's method [4]. Cyclohexanone (120 g) and absolute methanol (500 ml) were added to ethereal diazomethane prepared from 180 g of 1-methyl-1-nitrosourea, and then 5 g of calcined potassium carbonate was added. There was an immediate vigorous evolution of nitrogen. On the next day the reaction mixture had a yellowish color. Ether and alcohol were distilled off, and cycloheptanone was isolated by fractionation from a flask fitted with a column. The yield of cycloheptanone was about 65% on the amount of cyclohexanone taken; it had b.p. 177-179° (750 mm), d_4^{20} 0.9533; and n_D^{20} 1.4615. The literature [5] gives b.p. 178.2-178.8 (745 mm), d_4^{20} 0.9542; and n_D^{20} 1.4625.

The catalyst was prepared by impregnating pieces of active alumina with nickel nitrate solution, drying, calcining, and reducing with hydrogen at 350° in the catalysis tube; it contained 15% of finely dispersed nickel. A mixture of cycloheptanone vapor, ammonia, and hydrogen was passed over 50 ml of this catalyst at a measured rate: the space velocity of the ketone was 0.2 hour⁻¹, and the ammonia and hydrogen were taken in a 2-3-fold excess. The reaction products were condensed in an ice-cooled receiver. The duration of each experiment was 60 minutes.

The condensates were dried over solid potassium hydroxide, and the content of amine nitrogen was then determined by Francois' method [6]. Also the components of the condensate were separated and investigated. For this purpose the condensate was treated with dilute hydrochloric acid. The non-amines were separated and washed three times with water. The aqueous solution of amine hydrochlorides was combined with the washings and partially distilled. Non-amines were separated from the distillate by salting out with potassium carbonate. After being dried, the whole of the non-amines were fractionally distilled. The solution of amine salts remaining in the flask was saturated with solid caustic alkali. The free amines were separated, dried with solid potassium hydroxide and then with sodium, and fractionated.

The table gives the conditions of the reductive amination of cycloheptanone and the results obtained. The first four experiments had the object of finding the optimum temperature at which the condensate with the highest content of amine nitrogen is obtained. The experiments showed that this temperature was 190°. Rise in temperature above this level resulted in reduction both in the amount of condensate and in its content of amine nitrogen. Experiments 5-17 were carried out at 190° in order to establish how long the catalyst remain active.

TABLE

Reductive Amination of Cycloheptanone

Experiment	Temperature (°C)	Amounts taken for reaction			Yield of condensate		Content of amine nitrogen (%)
		Cycloheptanone (g)	Ammonia (g)	Hydrogen (liters at STP)	Total (g)	After drying (g)	
1	190	10	4.4	4.5	10.2	8.7	8.49
2	230	10	4.4	4.5	10.2	9.3	7.93
3	260	10	5.2	4.5	10.0	8.4	4.66
4	290	10	4.4	4.5	7.6	6.2	4.13
5	190	10	4.4	4.5	9.8	8.5	8.03
6	190	10	4.4	4.5	9.9	8.6	—
7	190	10	4.0	4.5	9.6	8.5	8.20
8	190	10	5.0	4.5	10.2	9.4	—
9	190	10	5.2	4.5	10.4	9.5	7.51
10	190	10	4.8	4.5	10.2	9.4	—
11	190	10	4.4	4.5	10.3	9.4	6.28
12	190	10	4.0	4.5	10.1	9.3	—
13	190	10	4.4	4.5	10.3	9.2	6.40
14	190	10	4.0	4.5	9.8	8.7	—
15	190	10	4.0	4.5	9.9	8.7	6.86
16	190	10	4.0	4.5	10.3	9.7	—
17	190	10	4.0	4.5	10.3	9.6	6.06

From 30 g of condensate from Experiments 1-4 we isolated 19.0 g of amines and 9.3 g of non-amines. Fractionation of the amines at 750 mm gave:

Fr. I.	b.p.	133-136°:	6.6 g containing 14.08% of amine nitrogen
Fr. II.	b.p.	136-145°:	1.9 g containing 13.33% of amine nitrogen
Fr. III.	b.p.	145-155°:	1.6 g containing 12.70% of amine nitrogen
Fr. IV.	b.p.	155-190°:	2.8 g containing 9.77% of amine nitrogen
Fr. V.	b.p.	190-220°:	1.9 g containing 9.05% of amine nitrogen
Fr. VI.	b.p.	220-270°:	1.2 g containing 5.96% of amine nitrogen
Residue			1.7 g

Fraction I had d_4^{20} 0.8645 and n_D^{20} 1.4586. Its hydrochloride melted at 203°, and its benzoyl derivative at 147°. On the basis of these results, Fraction I must be regarded as cyclohexylamine, for which the literature gives b.p. 133.5–134° [7], d_4^{24} 0.863 n_D^{24} 1.4575, hydrochloride m.p. 203–204° [8], benzoyl derivative m.p. 147° [9]; the nitrogen content for $C_6H_{13}N$ is 14.14%. Owing to lack of material it was not found possible to identify the other amine fractions of this condensate.

From 9.3 g of non-amines fractionation at 752 mm gave:

Fr. I. b.p.	161–177°: 3.5 g
Fr. II. b.p.	177–180°: 4.2 g; d_4^{20} 0.9539; n_D^{20} 1.4619
Residue	1.5 g

According to its properties, Fraction II was unchanged cycloheptanone.

From 65 g of the general condensate from Experiments 5–17, carried out at 190°, we isolated 31.7 g of amines and 29.2 g of non-amines. The amines, fractionated at 742 mm, gave:

Fr. I. b.p.	154–160°: 3.95 g containing 12.64% of amine nitrogen
Fr. II. b.p.	161–162°: 15.6 g containing 12.29% of amine nitrogen
Fr. III. b.p.	162–166°: 3.1 g containing 12.07% of amine nitrogen
Fr. IV. b.p.	166–185°: 0.95 g containing 11.44% of amine nitrogen
Residue	3.1 g

Fraction II had d_4^{20} 0.8701 and n_D^{20} 1.4642; its benzoyl derivative melted at 108–109°; its chloroplatinate contained 30.41% of platinum. Elementary analysis for this fraction:

Found	%: C 74.20; H 13.07; N 12.29
$C_7H_{15}N$. Calculated	%: C 74.25; H 13.37; N 12.38

These results for Fraction II correspond to cyclohexanemethylamine, for which the literature gives b.p. 162–164° [10], d_4^{20} 0.8702; n_D^{18} 1.4646; benzoyl derivative m.p. 107–108° [11]; according to the formula $2C_6H_{11}CH_2NH_2 \cdot 2HCl \cdot PtCl_4$, the chloroplatinate of this amine contains 30.69% of platinum.

From the residue from the distillation of the amines we prepared 1.8 g of a pure hydrochloride. A solution of this salt reacted with sodium nitrite with separation of a nitrosamine in the form of a reddish-brown oil. The nitrogen content of the salt was 5.11%, and its chloroplatinate contained 23.14% of platinum. The free base was isolated from the salt and was shown by Sivolobov's method [12] to have b.p. 286° (742 mm). These results show that we are dealing with a secondary amine of composition $(C_6H_{11}CH_2)_2NH$, i.e. 1,1-dicyclohexyldimethylamine. According to the formula $(C_6H_{11}CH_2)_2NH \cdot HCl$, the hydrochloride of this amine contains 5.70% of nitrogen, and a chloroplatinate of composition $2(C_6H_{11}CH_2)_2NH \cdot 2HCl \cdot PtCl_4$ contains 23.56% of platinum.

From 29.2 g of non-amines fractionation at 742 mm gave:

Fr. I. b.p.	140–177°: 2.08 g
Fr. II. b.p.	177–179°: 13.85 g; d_4^{20} 0.9508; n_D^{20} 1.4619
Fr. III. b.p.	179–181°: 0.83 g
Fr. IV. b.p.	181–183°: 5.1 g
Fr. V. b.p.	183–190°: 2.15 g
	0.2 g

In its properties Fraction II corresponded to cycloheptanone. When treated with sodium, Fraction IV yielded hydrogen; elementary analysis:

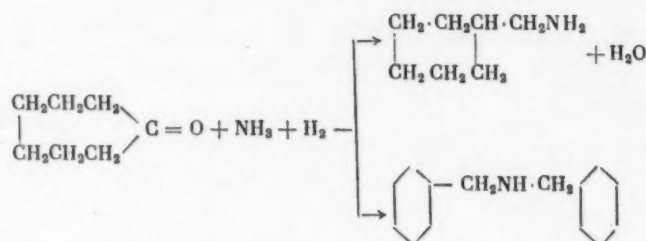
Found	%: C 73.56; H 12.30; O 14.14
$C_7H_{14}O$. Calculated	%: C 73.61; H 12.37; O 14.02

* As in original—Publisher's note.

The literature [13] gives the boiling point of cycloheptanol as 184–185° (755 mm). Fraction IV, therefore, corresponds to cycloheptanol, formed by reduction of the ketone.

DISCUSSION OF RESULTS

The experiment showed that, in the reaction of cycloheptanone with ammonia and hydrogen at 190–290°, the normal reaction product, cycloheptylamine, is not formed. In the course of the amination the seven-membered ring is transformed into a six-membered ring. The composition of the reaction products depends on temperature. The reductive amination of cycloheptanone at 190° gives a condensate which contains mainly cyclohexanemethylamine together with a little of the corresponding secondary amine. The formation of these amines proceeds via rupture of the seven-membered ring at a carbonyl-methylene bond in accordance with the scheme:



Raising the amination temperature above 190° results in the formation of a mixture of amines in which cyclohexylamine predominates. Judging from the boiling points of the fractions obtained and their amine-nitrogen contents, this mixture consists of various methylated cyclohexylamines, primary and secondary. Some of the original ketone does not react and, in experiments at 190°, some of it is reduced to the corresponding alcohol, cycloheptanol.

SUMMARY

1. An investigation was made of the reaction of cycloheptanone with ammonia and hydrogen in presence of nickel on active alumina at 190–290°.
2. It has shown that, under these conditions, the seven-membered ring contracts to a six-membered ring with formation of cyclohexanemethylamine.

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HETEROCHAIN POLYESTERS

COMMUNICATION 4. POLYESTERS OF 5,5'-SULFONYLDIVALERIC ACID

V. V. Korshak and S. V. Vinogradova

In a previous paper [1] we described polyesters formed by 5,5'-thiodivaleric acid with glycols of various structures. With the object of making a more detailed study of the effect of a sulfur atom in a molecule of a dicarboxylic acid on the properties of the polyesters derived from it, we synthesized and investigated polyesters of 5,5'-sulfonyldivaleric acid, i.e., of a dicarboxylic acid containing sulfur in the form of the sulfone group. The polyesters were prepared and investigated by procedures already described [2-4].

Table 1 gives our results for the polyesters formed by 5,5'-sulfonyldivaleric acid with various glycols. It will be seen that the melting points of these polyesters rise as the polymethylene chain of the glycol increases in length. An exception is found in the case of 1,5-pentanediol with an odd number of methylenes: its melting point is 2° below that of 1,4-butanediol. Comparison of the melting points of polyesters of 5,5'-sulfonyldivaleric acid with those of the corresponding polyesters of sebacic and azelaic acids indicates that the introduction of the SO₂ group into the chain of the dicarboxylic acid raises the melting points of the polyesters derived from it. Thus, polyethylene sebacate melts at 74° and polyethylene azelaate at 44°, whereas the polyester formed by ethylene glycol with 5,5'-sulfonyldivaleric acid melts at 82°. In subsequent members of the series this difference increases and becomes more than 20° for the comparison with the sebacid polyesters. Hence, the presence of the polar SO₂ group in the polymer is associated with a higher melting point.

It was of interest to compare the 5,5'-sulfonyldivaleric polyesters with the corresponding 5,5'-thiodivaleric polyesters, for sulfur is present in the main chain in both cases. Table 2 gives data for 5,5'-thiodivaleric polyesters, and comparison shows that their melting points are considerably lower than those of the corresponding 5,5'-sulfonyldivaleric polyesters (the melting points of the ethylene glycol polyesters are 25° and 82° respectively). The 5,5'-sulfonyldivaleric polyesters are much less soluble in benzene and alcohol. The form in which sulfur enters the polyester chain is therefore of great importance: sulfide sulfur lowers the melting point of a polyester, whereas the presence of a sulfone group causes a rise in melting point.

Lowering of the melting point of a polyester when an -S- linkage is present in the polymethylene chain can be explained by the increased flexibility of the polymer chain resulting from the absence of any substituents on the sulfur atom that can hinder free rotation with respect to the -C-S-C bonds. However, the presence on the sulfur atom of two bulky oxygen substituents already creates hindrance to rotation about the C-S bonds, and the chain therefore becomes more rigid. This fact, and also the much higher polarity of the SO₂ group, as compared with S, makes the polymer chain containing SO₂ groups more rigid, which is reflected in the melting point of the polymer.

It is characteristic also that polyesters of alkanediols with 5,5'-thiodivaleric acid are more crystalline than 5,5'-sulfonyldivaleric polyesters. Thus, determination on the consistometer of the temperatures of passage into the viscous and the mobile states indicated that the difference between these temperatures is only 1-2° for sebacic and 5,5'-thiodivaleric polyesters, indicating their high degree of crystallinity, whereas for 5,5'-sulfonyldivaleric polyesters this difference is greater (5-14°), indicating a lower degree of crystallinity. The lower degree of crystallinity of 5,5'-sulfonyldivaleric polyesters can be explained by the presence of the SO₂ group, which, being bulky, disturbs the compact packing of the polymer chains which is established when there are long polymethylene chains of a dicarboxylic acid of the sebacic type.

TABLE 1

5,5'-Sulfonyldivaleric Polyesters

No.	Glycol	Temperature (°C)		Solubility (g/liter)		Molecular weight by viscosity in creosol (K=1.29·10 ⁻⁴)	Appearance of polyester
		of melting	of passage into the viscous state	of passage into the mobile state	in alcohol	in benzene	
1	Ethylene glycol	82-86	75	81	—	—	Opaque solid
2	1,4-Butanediol	86-88	76	90	4.0	0.77	Opaque solid
3	1,5-Pentanediol	84-86	79	88	—	—	Opaque solid
4	1,6-Hexanediol	90-92	85	92	2.05	0.98	Opaque solid
5	1,10-Decanediol	98-101	97	102	1.65	1.8	Opaque solid
6	1,20-Eicosanediol	114-117	—	120	—	0.8	Opaque solid
7	1,2-Propanediol	65-68	—	—	—	—	Opaque solid
8	1,2-Propanediol	64-68	40	65	—	—	Opaque solid
9	1,3-Butanediol	32-35	28	43	—	2.1	Transparent substance
10	Diethylene glycol	64-66	—	—	—	—	Opaque substance
11	Diethylene glycol	65-68	24	73	—	—	Opaque substance
12	Triethylene glycol	24-27	—	—	—	—	Opaque substance

TABLE 2

5,5'-Thiodivaleric Polyesters

No.	Glycol	Temperature (°C)		Solubility in alcohol (g/liter)	Molecular weight
		of melting	of passage into the viscous state	of passage into the mobile state	
1	Ethylene glycol	25-28	—	6.2	3530
2	1,3-Propanediol	-39-36	—	6.3	2760
3	1,4-Butanediol	37-38	42.5	10.0	4720
4	1,5-Pentanediol	40-42	44	11.35	2580
5	1,6-Hexanediol	44-46	46	4.65	6600
6	1,10-Decanediol	54-57	60.5	3.3	5200
7	1,20-Eicosanediol	76-79	85.5	0.93	3560
8	1,2-Propanediol	-39 to -34	—	15.7	1970
9	1,3-Butanediol	-39 to -34	—	14.9	2250
10	Diethylene glycol	-39 to -34	—	7.95	1960
11	Triethylene glycol	-39 to -34	—	11.05	1600

The introduction of a methylene side group or ether linkage into the glycol molecule lowers the melting point of a 5,5'-sulfonyldivaleric ester appreciably, as compared with the corresponding α, ω -alkanediol polyester. Thus, the 5,5'-sulfonyldivaleric polyester of 1,2-propanediol melts at 65°, i.e., 17° below the melting point of the ethylene glycol polyester. The melting point of the diethylene glycol polyester is 18° lower than that of the 1,5-pentanediol polyester. Comparison of the melting points of the diethylene and triethylene glycol polyesters shows that accumulation of ether links in the glycol lowers the melting points of 5,5'-sulfonyldivaleric polyesters. In these respects 5,5'-sulfonyldivaleric polyesters are analogous to sebacic polyesters, which also have lower melting points when the polymethylene chain of the glycol is modified by the introduction of ether linkages or methyl side groups.

In conclusion, the authors express their indebtedness to R. Kh. Freidlina for kindly placing some 5,5'-sulfonyldivaleric acid at their disposal.

SUMMARY

1. Polyesters formed by 5,5'-sulfonyldivaleric acid with the following glycols were synthesized and investigated: the glycols $\text{HO}(\text{CH}_2)_n\text{OH}$ ($n = 2, 4, 5, 6, 10, 20$), 1,2-propanediol, 1,3-butanediol, diethylene glycol, and triethylene glycol.

2. The question of the effect of the structure of the original reactants on the physical properties of the polyesters derived from them is discussed on the basis of the results of the investigation.

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HETEROCHAIN POLYESTERS

COMMUNICATION 5. POLYESTERS OF DIGLYCOLIC ACID

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In previous communications we have examined polyesters prepared from dicarboxylic acids containing a methyl side group [1], a *p*-nitrophenyl side group [1], or a sulfide linkage [2]. Investigation of these polyesters showed that change in the structure of the acid affects the properties of the polyesters derived from the given acid. In continuation of these investigations it was of interest to determine the effect of an ether link in the original dicarboxylic acid molecule on the properties of the polyesters, for we have shown [3] that the presence of such a link in the glycol molecule has a considerable effect on the properties of the polyester. As a subject for the investigation we selected polyesters of diglycolic acid.

The procedures used in preparing and investigating the polyesters have been described previously [3, 4]. Our results are given in Table 1. Diglycolic polyesters No. 1-8, 10, 12, and 13 were prepared by heating the reactants in a stream of nitrogen for 6 hours at 100°, 2 hours at 120°, 4 hours at 140°, and 8 hours at 170°, after which heating was continued at a residual pressure of 1-2 mm for 5 hours at 170° and 16 hours at 200°. Polyesters No. 9 and 11 were prepared by heating the reaction mixture in a stream of nitrogen for 10 hours at 170° and 2 hours at 190°, after which heating was continued at a residual pressure of 1-2 mm for 2 hours at 190° and 18 hours at 200°.

DISCUSSION OF RESULTS

Comparison of the melting points of α, ω -alkanediol polyesters (see Table 1) shows that lengthening of the polymethylene chain of the glycol raises the melting point of the polyester. The only exception is the 1,4-butanediol polyester, which is higher-melting than its neighbors. Such anomalous behavior of 1,4-butanediol polyesters with respect to melting point was observed by us previously in the alkanedioic polyester series, e.g., glutaric, succinic, and adipic polyesters. A characteristic feature of the polyesters formed by diglycolic acid with 1,3-propane- and 1,5-pentane-diols is the fact that for a long time (3-4 weeks) after the reaction they remain liquid, solidifying only very slowly to waxlike substances. Consistometer measurements of the temperatures of transition into the viscous and mobile states for diglycolic polyesters showed that the transition temperatures of the 1,3-propanediol and 1,5-pentanediol polyesters are lower than those of the polyesters of the neighboring glycols containing even numbers of carbon atoms (thus for the polyester of ethylene glycol the temperature of transition to the viscous state is -20°, for that of 1,3-propanediol it is -42°, for that of 1,4-butanediol it is -70°, and for that of 1,5-pentanediol it is -14°). This indicates that the polymer chain of the 1,3-propanediol polyester is more flexible than that of the ethyleneglycol polyester, and the polymer chain of the 1,5-pentanediol polyester is more flexible than that of the 1,4-butanediol polyester.

As the number of methylene groups in the glycol increases in the polyesters of 1,6-hexanediol, 1,10-decanediol, and 1,20-eicosanediol, the polymer chain becomes constantly more regular with consequent rise in the temperature of transition to the viscous state. Introduction of an ether link into the glycol molecule (e.g. in the polyester of diethylene glycol) lowers the melting point of its diglycolic polyester, as compared with the corresponding α, ω -alkanediol polyester. Thus, the diglycolic polyester of diethylene glycol melts at 2°, whereas that of 1,5-pentanediol melts at 30°. In the case of ethylene glycol, introduction of a methyl side group to give 1,2-propanediol has no effect on the melting point of the polyester, but the temperature of

transition into the viscous state is lowered. In the case of 1,3-propanediol, introduction of a methyl side group to give 1,3-butanediol results in an appreciable lowering of the melting point of the polyester.

Diglycolic polyesters are only slightly soluble in benzene and alcohol, and are less soluble in benzene than in alcohol. The 1,6-hexanediol and 1,10-decanediol polyesters have the highest solubility in benzene (0.5-g samples of these polyesters dissolved completely in 10 ml of benzene).

In order to examine the effect of the presence of an ether link in the dicarboxylic acid molecule on the properties of the polyesters, the properties of the diglycolic polyesters may be compared with those of the corresponding glutaric polyesters, in that diglycolic acid differs from glutaric acid only in the presence of an ether oxygen in place of a methylene group.

We have shown previously [3] that the presence of an ether link in the glycol molecule results in lowering of the melting point of its polyester in comparison with that of the polyester of the corresponding α,ω -alkanediol. We explained this behavior by the increased flexibility of the polymer chain due to the presence of ether links. Analogy would suggest that the presence of an ether link in the dicarboxylic acid would also be accompanied by lowering of melting point of its polyesters as compared with the melting points of the polyesters of the corresponding dicarboxylic acid containing only methylene groups. However, comparison of the melting points of the corresponding polyesters of diglycolic and glutaric acids (see Table 2) shows that replacement of a methylene group of glutaric acid by oxygen does not lead to a lowering of the melting points of its polyesters, but, on the contrary, results in a rise in melting point. The rise is greatest for polyesters of the first "even" α,ω -alkanediols, ethylene glycol and 1,4-butanediol (for these polyesters the rise is 36–37°). As the polymethylene chain is lengthened, the difference diminishes: for 1,6-hexanediol it is 19° for 1,10-decanediol it is 16°, and for 1,20-eicosanediol it is 9°.

For polyesters of "odd" α,ω -alkanediols the difference in melting point is less. In our view, the higher melting points of diglycolic polyesters, as compared with glutaric polyesters, may be explained by the increased polarity of the carboxy groups resulting from the presence of the $-O-$ link in diglycolic acid. The higher polarity of the carboxy groups of diglycolic acid is confirmed by the fact that its dissociation constants are considerably higher than those of glutaric acid. Thus, the first and second dissociation constants of diglycolic acid at 25° are $1.1 \cdot 10^{-3}$ [5] and $37 \cdot 10^{-6}$

TABLE 1
Diglycolic Polyesters

No.	Glycol	Temperature (°C)		Solubility (g/liter)		Molecular weight by viscosity in benzene ($K=0.93 \cdot 10^{-4}$) and in <i>cis</i> -ol ($K=1.29 \cdot 10^{-4}$)	Appearance of polyester
		of melting	of transition to viscous state	in alcohol	in benzene		
1	Ethylene glycol	17–20	–20	0.25	—	3450	Thick liquid
2	1,3-Propanediol	29–32	–42	—	—	3940	Crystalline solid after long standing
3	1,4-Butanediol	67–70	70	3.95	0.8	4260	Opaque white
4	1,5-Pentanediol	30–33	–14	—	—	2600	Crystalline solid after long standing
5	1,6-Hexanediol	47–51	42	8.05	—	7400	Opaque white solid
6	1,10-Decanediol	61–64	65	2.5	0.5 g in 5 ml	7840	Opaque white solid
7	1,20-Eicosanediol	86–89	91	0.85	0.5 g in 5 ml	8350	Opaque white solid
8	1,2-Propanediol	17–21	–27	—	2.1	2440	Transparent rubbery
9	1,2-Propanediol	18–21	—	25.45	5.5	2790	Transparent rubbery
10	1,3-Butanediol	4–5	—	—	—	2270	Thick liquid
11	1,3-Butanediol	3–8	—	35.3	—	3810	Thick liquid
12	Diethylene glycol	2–6	–34	—	1.2	2790	Liquid
13	Triethylene glycol	–6 to –3	–10	—	—	3990	Liquid

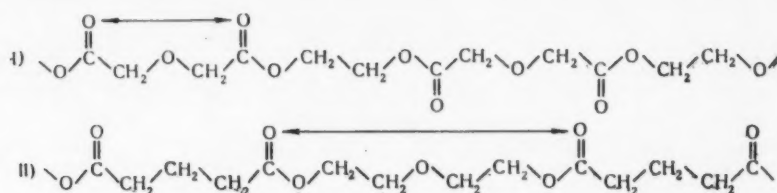
TABLE 2

Glutaric Polyesters

Glycol	M.p. (°C)	Solubility (g/ liter)		Mole- cular weight
		benzene	alcohol	
Ethylene glycol	-19 to -12	180.4	—	1200
1,3-Propanediol	35-36	—	7.3	1900
1,4-Butanediol	36-38	—	5.5	3600
1,5-Pentanediol	22-25	—	12.5	2700
1,6-Hexanediol	28-34	1.74	20.0	2200
1,10-Decanediol	55-58	171.2	1.5	3800
1,20-Eicosanediol	77-80	—	—	—
1,2-Propanediol	-19 to -12	182.3	—	1800
1,3-Butanediol	-19 to -12	—	—	2000
Diethylene glycol	-19 to -12	184.4	—	2500
Triethylene glycol	-19 to -12	195.5	—	2600

[6], whereas the corresponding constants of glutaric acid at 25° are only $4.75 \cdot 10^{-5}$ [7] and $2.9 \cdot 10^{-6}$ [8].

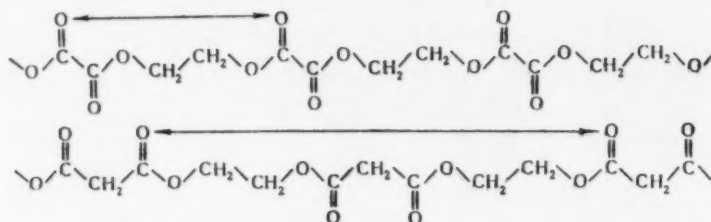
The presence of groups of higher polarity in the polymer chain makes it more rigid, which is manifested in the higher melting points of polyesters containing such chains. On the other hand, the question arises of why, in diglycolic polyesters, the rigidity due to the presence of polar carbonyl groups is not modified by the "softening" effect of the ether link, which is known to result in considerable lowering of melting point in the case of diethylene glycol and triethylene glycol polyesters. The explanation can be found by detailed examination of the structure of the polymer chains of diglycolic polyesters (e.g., the ethylene glycol polyester) and of the glutaric polyester of diethylene glycol:



The diagrammatic representation shows that the positions of the ether links are sterically nonequivalent in cases I and II. In the case of the diglycolic polyester, the ether link is blocked by bulky carbonyl groups, whereas in the case of the diethylene glycol polyester the bulky carbonyl groups are much more remote from the ether link, so that their blocking effect is less. The blocking of the ether link by carbonyl groups in diglycolic polyesters results in hindrance of free rotation of the C-O-C linkage in the diglycolic acid residue, so that free rotation cannot occur to the extent found in diethylene glycol polyesters, i.e., the softening effect of the ether link in the diglycolic polyester is suppressed by the proximity of large blocking groups. Thus, the higher melting points of diglycolic polyesters (as compared with glutaric polyesters) in spite of the presence of the ether link can be explained by 1) the increased rigidity of the polymer chain due to the presence of carbonyl groups of higher polarity, and 2) the stereochemical factor, which consists in the blocking of ether links in diglycolic acid residues by bulky carbonyl groups and therefore in hindrance to free rotation relative to the C-O-C linkage, i.e., reduction in the flexibility of the polymer chain.

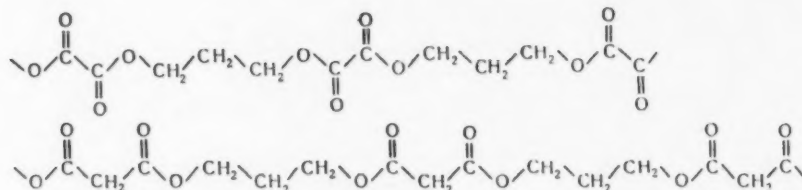
This examination of diglycolic polyesters and the explanation of the reduction in the flexibility of their chains by the blocking effect of carbonyl groups suggested to us that we might examine oxalic and malonic polyesters from the same point of view. Comparison of the graphical representations of the polyesters of these acids formed, for example, with ethylene glycol enabled us to explain the difference in the melting points of these polyesters. In fact, comparison of the structures of the polyethylene oxalate and polyethylene malonate chains shows that they differ with respect to the relative positions of the carbonyl groups and the ether

link. • Thus, in the oxalic polyester there is one methylene and one ether link between the carbonyl group (we are considering the upper part of the zigzag chain between consecutive carbonyl groups, i.e., between the arrow heads), whereas in the malonic polyester there are five groups — three methylenes and two ether — oxygens:



In the oxalic polyester, the oxygen of the ether link is blocked from one side by a bulky carbonyl group, but in the malonic polyester the ether link is separated from the carbonyl group by methylene groups. In the oxalic polyester, therefore, the effect of the ether link on the flexibility of the chain will be suppressed by steric hindrance due to the carbonyl group, whereas in the malonic ester the ether link exists under energetically more favorable conditions; also, there are more of them. On the basis of these considerations, the polymer chain of the malonic polyester should be more flexible than that of the oxalic polyester; moreover, it must not be forgotten that the rigidity of the oxalic polyester chain must be increased as a result of the strong interaction of the adjacent carbonyl groups.

The higher flexibility of malonic polyester chains is reflected in the fact that the melting point of polyethylene malonate is much lower than that of polyethylene oxalate. An examination of the polyesters of "odd" α, ω -alkanediols indicates that, in this case also, the higher melting point of the oxalic polyester [10] can be explained similarly. The structures of the oxalic and malonic polyesters of 1,3-propanediol can be represented as follows:



These structures indicate that, whereas in the oxalic polyester the carbonyl groups block the ether link, in the malonic polyester this does not occur, which explains the much lower melting point of polytrimethylene malonate.

SUMMARY

1. Diglycolic polyesters of the following glycols were synthesized and investigated: $\text{HO}(\text{CH}_2)_n\text{OH}$ ($n = 2-6, 10, 20$), 1,2-propanediol, 1,3-butanediol, diethylene glycol, and triethylene glycol.
2. The effect of the structures of the reactants on the physical properties of the polyesters obtained from them is discussed on the basis of the results obtained.

• The use of the term "ether" in the description of oxygen atoms in polyethylene oxalate and malonate chains is the author's, not the translator's. — Publisher.

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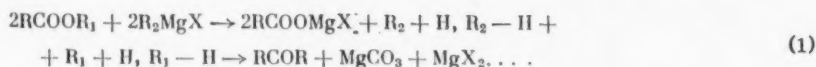
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BRIEF COMMUNICATIONS

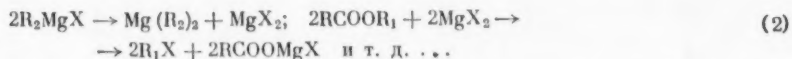
REACTION OF *tert*-BUTYLLITHIUM WITH ESTERS

A. D. Petrov, E. B. Sokolova, and Gao Chin-Lan

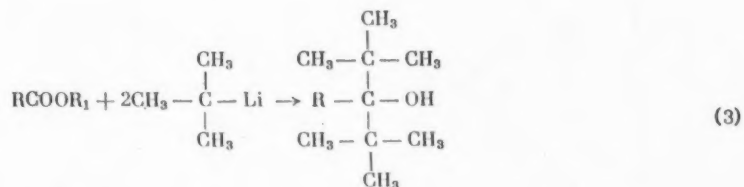
It was shown in a series of investigations [1] that *tert*-butylmagnesium halides react anomalously with esters with formation of symmetrical ketones, in which the radicals correspond to the radicals of the acids from which the esters are derived, of secondary alcohols (reduction products of these ketones), of secondary-secondary glycols, etc. The mechanism of this reaction — which in the case of esters of the lower acids proceeds at ordinary temperature (in ether) and in the case of the higher acids proceeds at higher (up to 100°) temperatures (in xylene) — was represented by the following schemes



or



The possibility of hydrolysis of the ester under these conditions was verified experimentally by heating heptyl palmitate with anhydrous magnesium chloride, as a result of which heptyl chloride was isolated [2]. It was established also [3] that, when magnesium was replaced by sodium, to which *tert*-butyl chloride and a butyric or isobutyric ester was added, only in the case of the isobutyric ester did reaction proceed normally with formation of 3-isopropyl-2,2,4,4-tetramethyl-3-pentanol in low yield (19%). However, in the case of the butyric ester, the only products were 2,2-dimethyl-3-hexanone and the corresponding secondary alcohol. In the present investigation we replaced sodium by lithium and moved from a one-stage synthesis to reaction in two stages. The condensation of the alkyl lithium with esters was carried out at a very low temperature (from -35° to -40°). These conditions ensured that reaction proceeded by the scheme of pure organometallic synthesis:



which contrasts with (1) and (2), in which reaction proceeded partly by free-radical and partly by ionic mechanisms, and very high yields of tertiary alcohols were obtained (see Table). The yield of alcohol fell as the length of the radical R increased and also when tertiary-tertiary glycols were prepared. A characteristic feature of this reaction is the complete absence of reductive side reactions, even in the case of reaction with

TABLE

Formula of alcohol obtained	Yield (%)	B.p. in °C (p in mm)	M.p. (°C)	n_D^{20}	d_4^{20}	MR		Found %			Calculated %			Yield of ketone	
						Found	Calc.	C	H	OH	C	H	OH	RCOR,	RCOR
$\begin{array}{c} \text{CH}_3 \text{ OH CH}_3 \\ \quad \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{C} - \text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \text{ H CH}_3 \end{array}$	85.3	116 (164)	51	—	—	—	—	75.15 75.14	14.04 13.97	11.2	74.87	13.97	11.8	—	—
$\begin{array}{c} \text{CH}_3 \text{ OH} \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \text{ CH}_2 \text{ C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	66.7	101 (22)	—	1.4542	0.8652	58.28	59.14	77.40 77.35	14.09 14.15	8.65	77.35	14.07	9.12	11.3	—
$\begin{array}{c} \text{CH}_3 \text{ OH} \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \text{ CH}_2 \text{ C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	88.1	78 (4)	—	1.4655	0.8853	58.40	59.14	77.50 77.40	14.00 14.08	9.00	77.35	14.07	9.12	1.1	—
$\begin{array}{c} \text{CH}_3 \text{ OH} \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \text{ CH}_2 \text{ C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	50.5	128 (7.5)	—	1.4569	0.8603	72.18	72.99	78.45 78.52	14.03 13.95	6.91	78.85	14.14	7.45	30.6	—
$\begin{array}{c} \text{CH}_3 \text{ OH} \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \text{ CH}_2 \text{ C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	24.6	165 (4)	—	1.4676	0.8698	90.20	91.00	80.93 80.85	13.62 13.66	5.77	80.78	13.72	6.03	12.0	1.3
$\begin{array}{c} \text{CH}_3 \text{ OH} \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \text{ CH}_2 \text{ C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	26.3	183 (2)	104 105	Molecular weight Found 330 Calculated 342.6	—	—	—	77.05 77.15	13.40 13.24	10.2	77.12	13.53	9.93	—	—

formic esters (cf. [4]). Ketones of the type RCOR were found, and then only in traces, only in the case of esters of very high molecular weight, such as undecenoic ester.

EXPERIMENTAL

The preparation of tert-butyllithium and its condensation with esters were carried out under the following conditions. In an atmosphere of nitrogen at a temperature of from -35° to -40° (external cooling with mixture of solid carbon dioxide and acetone), a solution of tert-butyl chloride in an equal volume of ether was added to a vigorously stirred mixture of finely cut lithium and dry ether. When the addition was complete, the reaction mixture was stirred further for 30 minutes. The temperature of from -35° to -40° was selected on the basis of preliminary experiments which showed that at -55° the condensation did not go, whereas at -20° the decomposition of the organolithium compound under the action of diethyl ether became very appreciable.

A solution of the ester in ether was added to the organolithium compound obtained, the amount of tert-butyllithium being double that required according to Equation (3). The cooling bath was removed, and stirring was continued for one hour. The reaction mixture was decomposed with ice, acidified with hydrochloric acid, and extracted with ether. Ether was distilled off, and the reaction product was treated with 15% alcoholic NaOH to remove unchanged ester by hydrolysis (the hydrolysis was omitted only in the experiment with ethyl formate). The product was then vacuum-fractionated through a column, and the fractions obtained were analyzed.

SUMMARY

1. It was shown that, unlike tert-butylmagnesium chloride, which reacts anomalously with esters, tert-butyllithium reacts normally at a temperature of from -35° to -40° with formation of tertiary alcohols and glycols in high yields.
2. The following were synthesized for the first time: 3-tert-butyl-2,2-dimethyl-3-nonanol, 3-tert-butyl-2,2-dimethyl-12-tridecen-3-ol, and 3,8-di-tert-butyl-2,2,9,9-tetramethyl-3,8-decanediol.

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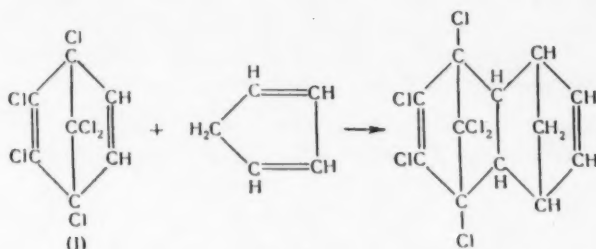
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PREPARATION OF 1,2,3,4,7,7-HEXACHLOROBICYCLO[2.2.1]HEPTA-2,5-DIENE
BY CONDENSATION OF HEXACHLOROCYCLOPENTADIENE WITH ACETYLENE

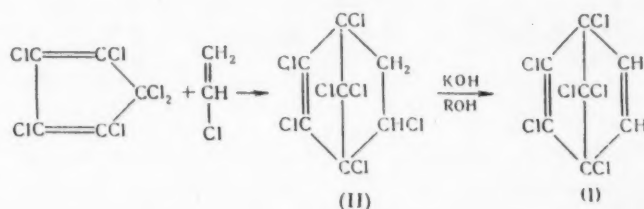
A. F. Plate and G. A. Tarasova

Hexachlorocyclopentadiene has recently found extensive application in the preparation of insecticides, in particular, aldrin, dieldrin, chlordan, and heptachlor [1]. For the synthesis of aldrin, one of the most important insecticides of this series, the reactants are hexachlorocyclopentadiene and bicyclo[2.2.1]hepta-2,5-diene, and oxidation of aldrin gives the insecticide dieldrin. A more active product than aldrin is its stereoisomer isodrin, which can be prepared by the diene synthesis from cyclopentadiene and 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (I):



When isodrin is oxidized to the corresponding epoxide, the product is the insecticide endrin a stereoisomer of dieldrin. It should be noted that the actual spatial configurations of these compounds have not yet been established.

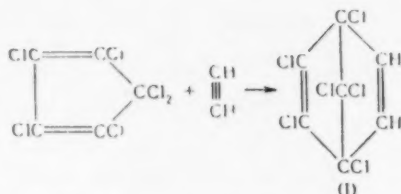
Hence, 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene is the starting material for the preparation of two active insecticides, isodrin and endrin, so that its synthesis is of great practical importance. According to patents of Shell Development Co. [2, 3], 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene may be prepared in two stages: heating of hexachlorocyclopentadiene with vinyl chloride at 2 atm at 120° for 48 hours gives 1,2,3,4,5,7,7-heptachlorobicyclo[2.2.1]hept-2-ene (II), from which hydrogen chloride is eliminated by the action of alcoholic alkali:



The Velsicol Chemical Corporation has patented a similar two-stage process [4], but the diene condensation is carried out at 200° for 14 hours. In the patent of Hymen and Co. [5] it is stated that (I) can be prepared in one stage by reaction between hexachlorocyclopentadiene and acetylene at 180° and 2-4 atm for 5 hours.

In the first three patents the following boiling points are given for (I): 128–145° (18 mm) [2, 3] and 128–130° (7 mm) [4]. The patent of Hymen and Co. [5] states that crystallization from hexane gave a solid of m.p. 332–334°, which was either 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene or its polymer. No other constants are given in these patents.

Working on analogy with the preparation of bicyclo[2.2.1]hepta-2,5-diene by the condensation of cyclopentadiene with acetylene under pressure [6], but under somewhat different conditions, we synthesized 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene by the condensation of hexachlorocyclopentadiene with acetylene in an autoclave:



Reaction was for 8–11 hours at an initial acetylene pressure of 15 atm and at 120–145°; yields of 16–46% of (I) were obtained.

We purified the 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene by fractionation through a column and recrystallization at low temperature from ethanol; it then had the following properties: f.p. -0.1° ; b.p. 125–126° (10 mm); n_D^{20} 1.5550; d_4^{20} 1.6606; MR Found: 57.76; Calculated for $C_7H_2Cl_6$ 2 MR 58.39; M (cryoscopically in benzene) Found 297.5; 303.8; Calculated for $C_7H_2Cl_6$ M 298.63. It follows from our results that the solid product of m.p. 332–334° referred to in the patent [5] as the product of the condensation of hexachlorocyclopentadiene with acetylene was not 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene.

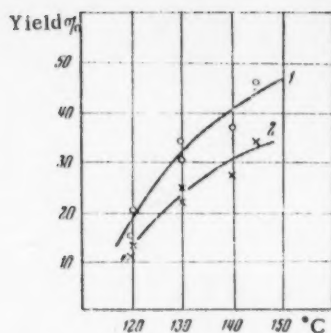
By condensation of our preparation of (I) with cyclopentadiene, N. N. Melnikov and L. G. Volfson prepared isodrin of m.p. 236° (the literature [2] gives 240–242°). Toxicological tests showed that it had high insecticidal activity.

EXPERIMENTAL

Experiments on the condensation of hexachlorocyclopentadiene with acetylene were carried out in an electrically heated 150-ml rotating steel autoclave. The hexachlorocyclopentadiene was obtained from the Research Institute of Fertilizers and Insectofungicides and was subjected to purification treatments, for it was found that impurities have an unfavorable effect on the course of reaction and the yield of condensation product. The following methods of purification were used: fractionation through a 30-plate column, chromatography on silica gel, and freezing out. The constants of the samples of hexachlorocyclopentadiene used in the work lay within the following limits: f.p. from $+8.0^\circ$ to $+10.3^\circ$; n_D^{20} 1.5647–1.5652; d_4^{20} 1.7070–1.7084. The literature gives: f.p. $+10.8^\circ$; n_D^{20} 1.5647 [7]; d_4^{25} 1.7035 [8].

For each experiment we took 20 g of hexachlorocyclopentadiene and 5 ml of a pentane fraction (b.p. 30–40°). The pressure of acetylene in the autoclave was brought up to 15 atm (about 15% in excess of the theoretical amount). Heating was continued for 8–11 hours, with a break overnight. Excess of acetylene was removed and the pentane fraction was distilled off; the residue was fractionated at 9–12 mm. The desired product was taken to be the fractions of b.p. 120–130° (12 mm); they had refractive indices n_D^{20} in the range 1.5562–1.5580. The relation of the yield of these fractions to the temperature of the experiment is shown in the figure (Curve 1).

Such fractions from different experiments were combined and fractionated through a 20-plate column having a glass filling, when 73% by weight of the material came over at 125–126° (10 mm). This narrow fraction had n_D^{20} 1.5550; d_4^{20} 1.6622; and f.p. -1.5° . The refractive index was not affected by two crystallizations from ethanol at -35° , but the density was lowered somewhat and the freezing point was raised. The 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene so obtained had the constants given above in the general discussion. It was a viscous faintly yellowish oil having a terpene odor:



Relation between yield of 1,2,3,4,7,7-hexachlorobicyclo [2.2.1]hepta-2,5-diene and temperature: 1) of wide fraction; 2) of pure product

Found %: C 28.41; 28.45; H 0.75; 0.77; Cl 70.68; 70.95 $C_7H_2Cl_6$. Calculated %: C 28.13; H 0.67; Cl 71.20

As it was shown that not less than 73% of a pure preparation of (I)' could be isolated from the wide fraction of b.p. 120-130° (12 mm), the yields of (I) obtained in the different experiments were recalculated accordingly. These results are given in the figure (Curve 2).

SUMMARY

1,2,3,4,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-diene, a starting material for the synthesis of the insecticides isodrin and endrin, was prepared by condensation of hexachlorocyclopentadiene with acetylene under pressure.

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DEHYDROGENATION OF PENTANE IN PRESENCE OF A MIXED ALUMINUM CHROMIUM POTASSIUM OXIDE CATALYST

N. I. Shuikin, E. A. Timofeeva, and V. M. Kleimenova

In previous papers [1,2] we have described investigations on the dehydrogenation of pentane in presence of an alumina-chromia-magnesia catalyst of composition 45 : 30 : 25 : moles % of Cr_2O_3 , Al_2O_3 , and MgO . At 500° and 550° pentane gave catalyzates containing 20–26% of pentenes, mainly 2-pentene. However, this catalyst was not very stable, so that its activity fell comparatively rapidly. Simultaneously with the investigation of the dehydrogenation of pentane, we carried out work on obtaining an active catalyst and determining the optimum conditions for the dehydrogenation of isopentane into isopentenes. As a result we succeeded in finding a catalyst consisting of Al_2O_3 , Cr_2O_3 , and K_2O (90.7 : 5.6 : 3.7 moles %) and having a high dehydrogenating power [3], and we developed a method for the preparation of this catalyst. In presence of this catalyst at 527° we obtained catalyzates containing 38% of isopentenes (33% calculated on the amount of isopentane taken) from isopentane. The activity of the catalyst did not fall after more than 200 hours of work. We have now investigated the activity of this aluminum chromium potassium oxide catalyst for the dehydrogenation of pentane and have studied the compositions of the catalyzates obtained.

EXPERIMENTAL

The dehydrogenation of pentane was carried out under the conditions that we used for the dehydrogenation of isopentane [3]. The catalyst, amounting to 30 ml (19.1 g), was placed in a layer of length 90 mm in the glass catalysis tube, internal diameter 18 mm. Pentane (b.p. 36.0–36.5° at 760 mm; n_D^{20} 1.3577; d_4^{20} 0.6263) was fed to the tube from a spray buret at a space velocity of 0.5 hour⁻¹ in 10 ml (6.27 g) portions. The temperature of the experiment was 527°. The receiver was cooled with solid carbon dioxide. The temperature was measured with a chromel-alumel thermocouple placed in the layer of catalyst. After every four portions of pentane (40 ml), the catalyst was regenerated by air oxidation for 4–5 hours at 550°.

The combined catalyzate (average yield 88.0%) from numerous experiments carried out under these conditions had the following properties: n_D^{20} 1.3682; d_4^{20} 0.6363; Margosches iodine value 115.0; content of unsaturated hydrocarbons 31.7% (calculated on original pentane: 28.0%). In the catalytic treatment of each portion of pentane (6.27 g), 1250 ml of gas was liberated on the average, and this had the following composition: hydrogen 71.1%, unsaturated hydrocarbons 3.9%, paraffins 25%. The pentane catalyzate (270 g) was fractionated through a 40-plate column. The properties of the fractions obtained are given in the table.

TABLE

No Fraction	Boiling range (°C at 760 mm)	Amount g	n_D^{20}	d_4^{20}	Iodine value	Content of unsaturated hydrocar- bons (% by wt)
I	25.5–28.5	18.8	1.3580	—	—	—
II	28.5–37.0	172.2	1.3655	0.6336	109.8	30.3
III	37.0–39.3	65.7	1.3670	0.6365	130.4	35.9
IV	39.3–46.8	2.5	1.4255	—	—	—
Residue	—	6.7	1.4605	—	98.9	27.2

Investigation of Catalyze Fractions

Fraction I. After bromination of 14.6 g of Fraction I and fractionation of the products we isolated 5.2 g of isopentane (b.p. 27.0–30.0°; n_D^{20} 1.3540; d_4^{20} 0.6200), 20.9 g of dibromopentanes boiling mainly in the range 60–70° (14 mm) and having n_D^{20} 1.5110 and d_4^{20} 1.6770, and 0.5 g of a crystalline substance from the residue in the flask (1.05 g), which melted at 86.8° after two crystallizations from alcohol; this melting point corresponds to 1,2,4,5-tetrabromopentane (the properties of di- and tetra-bromopentanes are given in a previous communication [1]). Fraction I, therefore, consisted of isopentane, pentenes, and 1,4-pentadiene.

Fraction II. On the basis of data obtained by Raman spectrum investigation*, this fraction consisted of 70% of pentane, 4% of 1-pentene, 18% of cis-2-pentene, and 8% of trans-2-pentene.

Fraction III. This was investigated by the same spectrographic method; it contained 70% of pentane, 2% of 1-pentene, 20% of cis-2-pentene, and 8% of trans-2-pentene.

Fraction IV. Bromination of 2.1 g of this fraction resulted in the isolation of a crystalline substance (2.0 g), m.p. 114.5° after two crystallizations from alcohol:

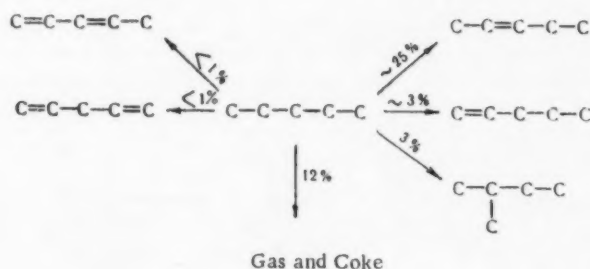
Found %: C 15.52; 15.63; H 2.12; 1.97; Br 82.32; 82.39 $C_5H_8Br_4$. Calculated %: C 15.49; H 2.08; Br 82.43

On the basis of the boiling range of the fraction, the melting point of its bromide, and the analysis of the latter, we may consider that the presence of piperylene in the fraction is proved.

Residue. This contained aromatic (positive formolite test) and unsaturated hydrocarbons, and 6.6 g of it was distilled from a small flask with a column, 4.5 g of a substance boiling over the range 46.8–80.0° and having n_D^{20} 1.4290 being collected. After separation of benzene and unsaturated hydrocarbons by adsorption on silica gel, we isolated 0.7 g of a substance having b.p. 36.0–50.5°, n_D^{20} 1.3840, and aniline point 44.1°. It is probable that this fraction contained cyclopentane as well as pentane (properties of pentane — b.p. 36.07°, n_D^{20} 1.3575, and aniline point 71.7°; properties of cyclopentane — b.p. 49.26°, n_D^{20} 1.4065, and aniline point 16.6° [4]). We showed previously [2] that cyclopentane is present also in the pentane catalyze obtained in presence of an alumina-chromia-magnesia catalyst.

Hence, in the pentane catalyze obtained in presence of an aluminum chromium potassium oxide catalyst, apart from unchanged pentane, we found % by weight on the catalyze): 17% of cis-2-pentene, 7% of trans-2-pentene, 3% of 1-pentene, 4% of pentenes of undetermined structure, 3% of isopentane, and 0.2% of piperylene. The catalyze contained also 1,4-pentadiene (less than 1%) and possible benzene and cyclopentane.

Our results show that the main reactions undergone by pentane under our conditions are as follows (% by weight on the original amount of pentane):



The conversion of pentane was about 44%.

* Raman spectrum analysis of the fractions was carried out by Yu. P. Egorov, to whom we express our thanks.

SUMMARY

1. The hydrogenation of pentane was investigated in presence of an aluminum chromium potassium oxide catalyst at 527° at a space velocity of 0.5 hour⁻¹.

2. It was shown that under these conditions dehydrogenation of pentane proceeds fairly smoothly with formation of a catalyzate containing 31% of pentenes (28% of 2-pentene and 3% of 1-pentene) and a very small amount of pentadienes.

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**In Russian.

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SELECTIVE DEMETHYLATION OF *n*-ALKANES OVER A SKELETAL NICKEL-ALUMINUM CATALYST

N. I. Shuikin and M. I. Cherkashin

In the hydrogenolysis of alkanes, the positions of C—C bond rupture are to a large extent determined by the selectivity of the catalyst and certain kinetic factors. Thus, Haensel and Ipatieff [1] showed that, in presence of nickel deposited on kieselguhr at 240–280°, hydrogenolysis of the bonds attaching methyl side groups to the main skeleton may occur in the case of isoparaffins. The same authors studied the demethylation of mixtures of various branched hydrocarbons under a pressure of hydrogen [2]. As Kazansky pointed out [3], the selective action of some catalysts with respect to C—C bond rupture is due to the nonequivalence of the bonds in the compounds. An example that confirms this conclusion is the vigorous decomposition of 3-methylpentane in presence of nickel deposited on alumina [4], even at 260°.

There is a reference in the literature [5] to unpublished work of Haensel, Linn, and Ipatieff, who obtained *n*-C₁₅, *n*-C₁₄, and *n*-C₁₃ hydrocarbons and methane in the hydrogenolysis of hexadecane. The reaction conditions were not indicated. Such a difference in the behavior of nickel deposited on kieselguhr and nickel on alumina, and also the absence of published work on the hydrogenolysis of *n*-alkanes, prompted us to study the behavior of hexane (b.p. 68° (760 mm); n_D^{20} 1.3750; d_4^{20} 0.6594) and heptane (b.p. 98° (760 mm); n_D^{20} 1.3877; d_4^{20} 0.6836) over a skeletal (Raney-type) nickel-aluminum catalyst prepared by the method described by one of us [6].

EXPERIMENTAL

The experiments were carried out in a flow system at 200°. Hexane was passed in 68-g portions and heptane in 48-g portions at a space velocity of 0.06 hour⁻¹ in excess of hydrogen. The reaction products were fractionally distilled through a 40-plate column. On the basis of fractionation curves (Figures 1 and 2) we isolated narrow fractions, which were either individual substances or mixtures, and determined their physical properties. The gases were analyzed in a VTI apparatus and with a chromathermograph. The results are given in Tables 1 and 2.

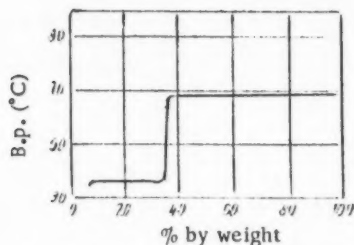


Fig. 1. Fractionation curve of hexane catalyze.

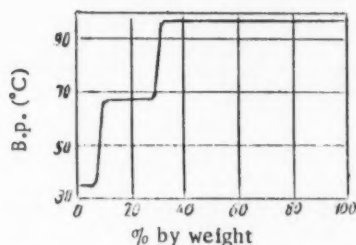


Fig. 2. Fractionation curve of heptane catalyze.

It will be seen from Tables 1 and 2 that about 30% of hydrogenolysis products were obtained in the

TABLE 1

Products of the Catalytic Hydrogenolysis of Hexane

Frac- tion	Properties of fraction			Yield (% on cataly- zate)	MR		Hydrocarbon isolated
	Boiling point at (758 mm)	n_D^{20}	d_4^{20}		found	calc.	
I	до 18	1.3493 (4.5°)	—	8.1	—	—	—
II	35.6—36	1.3574	0.6267	24.8	25.24	25.29	Pentane
III	68.6—68.8	1.3752	0.6596	61.9	29.92	29.91	Hexane
IV	Residue	—	—	3.2	—	—	—

catalyzates. The yields of catalyzate were 53.1% and 68% respectively. The main hydrogenolysis product of hexane was pentane. The gaseous products consisted entirely of hydrogen (41.8%) and methane (58.2%). The catalyzate obtained in the experiment with heptane contained both hexane and pentane. The outgoing gases consisted of methane (46%) and hydrogen (54%). From the spiral trap cooled with solid carbon dioxide slight warming liberated a gaseous substance found by chromatographic analysis to be butane (44%) and propane (22%), the remaining 34% being pentane. We have thus established that successive selective demethylations of n-alkanes occur over a skeletal nickel-aluminum catalyst according to the scheme:

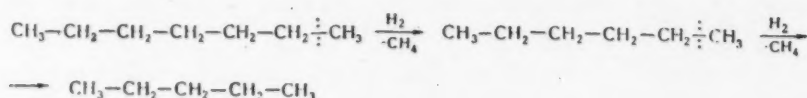


TABLE 2

Products of the Catalytic Hydrogenolysis of Heptane

Frac- tion	Properties of fraction			Yield (% on cataly- zate)	MR		Hydro- carbon isolated
	B.p. (°C at 757 mm)	n_D^{20}	d_4^{20}		found	calc.	
I	34.8—36.3	1.3565	0.6262	8.3	25.21	25.29	Pentane
II	67.9—68.3	1.3745	0.6584	20.7	29.93	29.91	Hexane
III	97.5—97.7	1.3880	0.6835	66.3	34.51	34.51	Heptane
IV	> 97.7	1.4012	—	1.2	—	—	—
V	Residue	—	—	2.0	—	—	—

The presence of only methane in the out-going gases and of small amounts (4 ml) of butane and propane in the gases condensed in the trap in the heptane experiments provides further confirmation of this scheme.

The results show that a skeletal nickel-aluminum catalyst has the specific power to bring about selective demethylation of n-alkanes.

SUMMARY

1. The destructive hydrogenation of hexane and heptane was investigated over a skeletal nickel-aluminum catalyst at 200°.
2. It was shown that hydrogenolysis of hexane gives pentane and that of heptane gives hexane and pentane.

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ORIGINAL ARTICLES

1. The Effect of the Diet on the Blood Sugar in the Normal Adult

2. The Effect of the Diet on the Blood Sugar in the Normal Adult

3. The Effect of the Diet on the Blood Sugar in the Normal Adult

4. The Effect of the Diet on the Blood Sugar in the Normal Adult

5. The Effect of the Diet on the Blood Sugar in the Normal Adult

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35. The Effect of the Diet on the Blood Sugar in the Normal Adult

USE OF ANION-EXCHANGE RESINS FOR THE REMOVAL OF SUBSTANCES ACCOMPANYING LEVOGLUCOSAN IN THE PRODUCT OF THE VACUUM THERMODEGRADATION OF CELLULOSE

N. M. Merlis, O. P. Golova, K. M. Saldadze, and I. I. Nikolaeva

The isolation of levoglucosan in quantitative yields from the thermodecomposition products of glucose, cellulose, starch, wood, etc. is a complex problem. The use of crystallization and distillation methods is associated with considerable losses of the anhydro sugar. For the isolation of pure substances from complex mixtures, the use of anionites (anion-exchange resins) has found wide application and they can be employed effectively in various technological processes. We set ourselves the task of applying anionites for the removal of substances accompanying levoglucosan in the product of the vacuum thermodegradation of cellulose.

EXPERIMENTAL

According to preliminary results, the main product, levoglucosan, is accompanied by acids, carbonyl-containing compounds, lactones, and phenols. The presence of free acidity and of substances giving acids under the influence of an alkaline medium (carbonyl compounds, lactones) prompted us to try the use of anionites. We used the following brands of anionite: EDE-10, AN-2F, AN-1, and H-O in the OH form.

TABLE 1*

Experiment	Brand of anionite	Loss of levoglucosan (%)	M.p. of the levoglucosan (°C)
1 ^a	N-O	1.0	171-173
2 ^a	AN-2F	2.0	177-180
3 ^a	EDE-10	0	176-178
10	EDE-10	1.6	180.5-181
14	AN-1	1.4	173-178

We first established the losses of pure levoglucosan on the anionites by passing 10 g of levoglucosan, m.p. 176-178°, as a 10% aqueous solution through 100 ml of swollen anionite and then eluting with water. It was found that in all cases the losses of levoglucosan were about 2% for 100 ml of anionite (Table 1).

Results on the use of anionites EDE-10, AN-2F, AN-1, and H-O for the purification of the thermodegradation product that we call "technical levoglucosan" are given in Table 2. The contents of levoglucosan in the original and purified materials were characterized arbitrarily by the increase in the

amount of reducing substances RS after hydrolysis, determined by Bertrand's method. Technical levoglucosan (usually 20 g) was passed through the anionite in the form of a 20% solution. This concentration corresponded approximately to 10% of levoglucosan. Table 2 shows that the best results, from the point of view of removal of substances accompanying levoglucosan, were obtained by the use of anionite EDE-10.

* The filtrate was collected in four fractions (100 ml, 100 ml, 200 ml, and 200 ml). Completion of elution of levoglucosan was checked by 1) separate vacuum evaporation of the fractions (Experiments 1a-3a) and 2) refractive index measurements on the fractions (Experiments 10 and 14); the latter fractions were then combined and evaporated together.

TABLE 2•

Experiment	Brand of anionite	Volume of anionite (ml)	Loss of levoglucosan (%)	Content in residue (%) of	
				RS calculated as glucose	levoglucosan
3	EDE-10	100	4.12	6.50	84.49
2	AN-2F	100	5.85	16.60	67.98
1	N-O	100	1.0	12.69	68.81
12	AN-1	200	8.2	9.7	78.93

before hydrolysis calculated as glucose

In view of the inadequacy of anionite EDE-10 for the purpose of removing colored impurities, in further work we used it in conjunction with the decolorizing anionite AN-1. In order to establish the maximum degree of purification obtained with the aid of these anionites, we used five successively connected anionite columns (the first two containing AN-1 and the others EDE-10) each containing 100 ml of anionite. After each column, starting with the second, the eluent was evaporated down and passed through the next column as a 20% solution until the levoglucosan content of the purification product no longer increased (Table 3).

TABLE 3

Experiment	Brand of anionite	Volume of anionite (ml)	Content in starting material (%) of		Content in purification product (%) of		Loss of levoglucosan (%)	[α] of purification product (degrees)	pH of filtrate
			RS calculated as glucose	levoglucosan	RS calculated as glucose	levoglucosan			
13	AN-1	200	12.05	74.37	5.32	84.47	7.44	-45.5	4.8
13	EDE-10	100	5.32	84.47	2.70	92.30	0	-49.7	6.7
13	EDE-10	100	2.70	92.30	2.07	96.74	0	-55.0	6.8
13	EDE-10	100	2.07	96.74	0.45	96.48	2.2	-54.3	—

The purity of the product at various stages of purification was characterized by the content of reducing substances before hydrolysis, calculated as glucose, by the levoglucosan content, by specific rotation, and also by qualitative reactions for the presence of aldehydes, hydroxy aldehydes, ketones, and phenols. The product isolated from technical levoglucosan with the aid of anionites AN-1 and EDE-10 was a white crystalline substance that smeared slightly when rubbed; m.p. 100–110°. Its levoglucosan content was 96.48% and its RS content, calculated as glucose, was 0.45%. It was shown that it contained hydroxy aldehydes (positive reaction with Benedict's reagent) and ketones containing the grouping $-\text{CH}_2-\text{CO}-\text{CH}_2-$ (positive reaction with salicylaldehyde). The product did not contain acids, aldehydes, substances that react with Schiff's reagent, and phenols. As a result of passage of the solution through the anionite, carbonyl compounds were removed to an extent of not less than 95%. In all, up to 23% of impurities (calculated on the original amount of the technical product) were removed. The yield of the purification product was about 70%. Investigation of substances accompanying levoglucosan and not removed by passage through anionites is continuing.

The use of anionites gave satisfactory results in the removal, under similar conditions, of substances accompanying levoglucosan in the thermodecomposition product of β -D-glucose [1]. It may be assumed that the results of the present work can be applied to the isolation of anhydro sugars from the pyrolysis products of other substances, such as wood, cellulignin, etc.

* The original substance contained 22.5% of RS and 54.63% of levoglucosan.

SUMMARY

1. A study was made of the possibility of removing substances accompanying levoglucosan in the product of the vacuum thermodegradation of cellulose with the aid of anionites.

2. It was shown that, by the use of the anionites AN-1 and EDE-10 in combination with one another, acids and phenols can be removed completely and carbonyl compounds to the extent of not less than 95% (in all, 23%; calculated on the original amount of technical product, of substances accompanying levoglucosan were removed). In this way the levoglucosan content can be raised from 74% to 96%.

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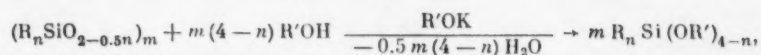
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LETTERS TO THE EDITOR

PREPARATION OF ALKOXYALKYLSILANES FROM ORGANOSILOXANES

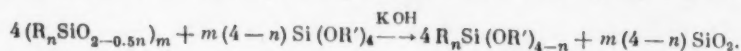
Dear Editor:

We have developed new methods of synthesizing alkoxyalkylsilanes from organosiloxanes. They are based on the scission of linear or cyclic organosiloxanes with alcohols in presence of potassium or sodium hydroxide or alkoxides as catalyst, in accordance with the general equation:

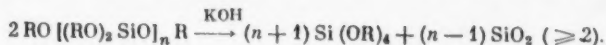


in which $\underline{n} = 1, 2, 3$; \underline{m} may vary over a wide range; R represents like or different hydrocarbon radicals.

The synthesis is carried out under conditions ensuring the removal of water formed from the sphere of reaction. In the case of alcohols boiling above 100°, this is attained by boiling a mixture of the alcohol and the organosiloxane (in some cases with addition of toluene or benzene) under a reflux condenser fitted with a water-removing trap until water ceases to separate. In the case of alcohols boiling below 100°, reaction is carried out in presence of a water-removing agent, the best of which is a suitable alkyl orthosilicate (apart from the cases in which $R' = CH_3$ and $i-C_3H_7$, ethyl orthosilicate is generally suitable). The alkoxyalkylsilane formed is isolated by fractional distillation of the reaction mixture. Alkoxyalkylsilanes are formed also by direct distillation of a mixture of linear or cyclic organosiloxanes with $Si(OR)_4$ in presence of alkaline catalysts:



The same reaction can be applied in the depolymerization of polyalkoxysiloxanes, when excellent yields are obtained:



By the above-indicated methods we have synthesized a whole series of compounds of the type $R_nSi(OR)_{4-n}$, in which R' contains 1-12 carbon atoms; yields of 50-90% were obtained.

Details of the results will be published shortly.

Institute of Silicate Chemistry of
the Academy of Sciences of the USSR

M. G. Voronkov
Received May 17, 1957

EXACT METHOD OF DETERMINING RELATIVE ADSORPTION COEFFICIENTS

Dear Editor:

As in the approximate method of determining relative adsorption coefficients z_r (in which r is the number assigned to a substance) and true rate constants k of catalytic reactions of a defined type in a flow system [1], in the exact method the starting point is Equation (19) in [1], which gives n equations of the form.

$$K + \sum_{r=2}^{r=n} [(A_{n1} + A_{nr}) \ln(1 - m_r + m_n) z_r = m_n,$$

in which m is the number of moles of the first substance transformed per minute and n are the numbers assigned to the experiments ($1 \leq n \leq r$), which are distinguished by the initial space velocity of the components A_{nr} . If we carry out experiments with binary mixtures so that $A_{11} = N_1$, $A_{21} = N_2 P_2$, $A_{31} = N_3 P_3$, $A_{22} = N_2(1 - P_2)$, $A_{33} = N_3(1 - P_3)$, and the remaining $A_{nr} = 0$, (P is the mole fraction of the original substance ($r = 1$) in the mixture), we obtain a linear system of equations with a determinant D . The solution required is $K = \Delta_1/D$; $z_2 = \Delta_2/D$, $z_3 = \Delta_3/D$, in which

$$\begin{array}{l} 1, a, a \\ D = 1, b, s \\ 1, c, t \end{array}$$

and Δ_1 , Δ_2 , and Δ_3 are similar determinants in which the first, second, and third columns are respectively replaced by columns of free terms m_1 , m_2 , and m_3 : $\underline{a} = N_1 \ln(1 - m_1/N_1) + m_1$, $\underline{b} = N_2 \ln(1 - m_2/N_2 P_2) + m_2$, $\underline{c} = N_3 P_3 \ln(1 - m_3/N_3 P_3) + m_3$, $\underline{s} = N_2 P_2 \ln(1 - m_2/N_2 P_2) + m_2$, $\underline{t} = N_3 \ln(1 - m_3/N_3 P_3) + m_3$. After being simplified, the determinants can be expanded or used in accordance with the usual rules of the theory of determinants. The solution is exact.

A. A. Balandin

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